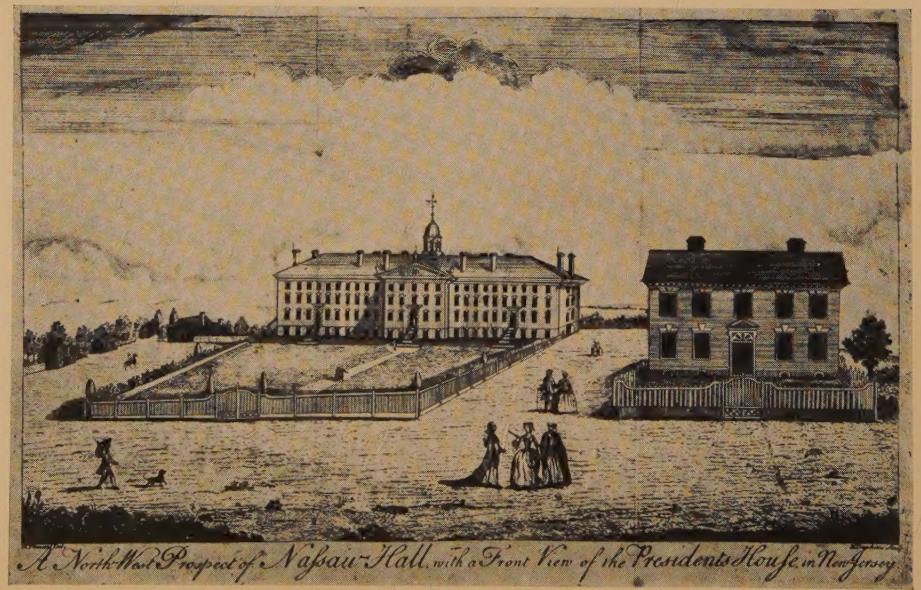
LECTURES ON COMBUSTION

By JOSEPH PRIESTLEY
and JOHN MACLEAN

540.1
P933

LECTURES ON COMBUSTION



NASSAU HALL IN COLONIAL DAYS

PALMER LIBRARY
CONNECTICUT COLLEGE
NEW LONDON, CONN.

CONSIDERATIONS ON THE DOCTRINE OF PHLOGISTON, AND THE DECOMPOSITION OF WATER

BY

JOSEPH PRIESTLEY, LL.D., F.R.S.

—*AND*—

TWO LECTURES ON COMBUSTION AND AN EXAMINATION OF DOCTOR PRIESTLEY'S CONSIDERATIONS ON THE DOCTRINE OF PHLOGISTON

BY

JOHN MACLEAN, M.D.
Professor of Mathematics and Natural Philosophy in the College of New Jersey (Princeton)

EDITED, WITH A SKETCH OF THE LIFE AND LETTERS OF DOCTOR MACLEAN,

BY

WILLIAM FOSTER, PH.D.
Professor of Chemistry, Princeton University

1929

PALMER LIBRARY
CONNECTICUT COLLEGE
NEW LONDON, CONN.

540.1
P933

PRINTED AT THE PRINCETON UNIVERSITY PRESS
PRINCETON NEW JERSEY, U. S. A.

FOREWORD

"THE finding of one generation will not serve for the next. It tarnishes rapidly except it be preserved with an ever-renewed spirit of seeking." This thought from a recent lecture of Professor A. S. Eddington may well serve to link the findings of Princeton's first professor of chemistry with the dedication, in 1929, *of Princeton's new laboratory of chemistry. The decision to commemorate the opening of a new laboratory by a republication of the contributions of Professor John Maclean to modern chemistry in the days of its infancy at the close of the eighteenth century, springs from a continuity in the scientific spirit of search which animated alike Maclean and his successors in the Department of Chemistry at Princeton in this twentieth century. A decade of vision and of hope on the part of those responsible for chemistry is now translated into a reality. From the new building new findings, new discoveries, new ideas will doubtless issue*

136665

to keep bright the tradition of progress in scientific truth which Maclean initiated at Princeton.

The test of each new contribution to chemical theory is ultimately made in the laboratory. The record of such a test of the phlogiston theory is contained in the following pages, and history has shown that Maclean's broad conclusions were justified. "I am of opinion," wrote Maclean to a former president of Princeton, "that it is impossible for me to require even a slight knowledge of chemistry without either making experiments or seeing them performed, and that to become proficient in the science it will require much practice as well as extensive reading. The necessity there is for seeing or making experiments proceeds chiefly from the nature of chemistry." Did Maclean ever dream of the future demands that this necessity for experiments in chemistry would produce? For the courage displayed in meeting those demands the Board of Trustees of Princeton University deserve the thanks of all chemists. Lacking a donor for the building, they have expended their capital resources with great liberality. To ensure that the spirit of research shall prosper in the new laboratory, loyal alumni, friends of the University, and scientific foundations have generously endowed the research activities to be prosecuted

therein. The members of the Department of Chemistry welcome this opportunity to express publicly our thanks and gratitude.

To Professor William Foster, the editing of this book and the preparation of the sketch of Maclean's career have been a labor of love, which will bring, however, its reward of appreciation from chemists generally. To Mrs. Marion Eppley of Newport, R.I., who responded gladly to the proposal to defray the expenses of the publication, a grateful expression of thanks is offered.

May the vivifying influence of Maclean in the early days of science in Princeton be an inspiration to those who now follow him in the tasks of teaching and seeking in chemistry.

HUGH S. TAYLOR.

Princeton, N. J., July 1929.

DR. JOHN MACLEAN

BY

WILLIAM FOSTER

Professor of Chemistry, Princeton University

JOHN MACLEAN, M.D., the first professor of chemistry in the College of New Jersey (Princeton), and according to the late Dr. Edgar F. Smith one of the most eminent chemists in the country at the close of the eighteenth century, was born in Glasgow, March 1, 1771, and was therefore a contemporary of Davy, Dalton, Priestley, Lavoisier, Berzelius, Avogadro, and of other very eminent chemists. His father, for whom he was named, was a surgeon of note, who was present at the capture of Quebec from the French, and he was the third man to scale the formidable heights of Abraham. His mother was Agnes Lang, of Glasgow.

While very young he lost both of his parents, whereupon George Macintosh, a gentleman of rare worth, became his guardian. It is of interest to note that he was the father of Charles Macin-

tosh, F.R.S., a wealthy chemical manufacturer who invented the waterproof cloth.

Young Maclean received his early education at the Glasgow Grammar School and in the University, which he entered before he was thirteen years of age, thus indicating that he was a precocious lad. This is borne out by the fact that he was awarded several premiums in school and in the University. It appears that he was much interested in the classics, particularly in Latin, and in later years he wrote to his son, John Maclean, Jr., who became the tenth president of Princeton, as follows: "Be assured, that notwithstanding what ignorant and lazy people say, it is a matter of great consequence for every gentleman or professional man to be a good classical scholar."

At the University he gave close attention to chemistry, mathematics and natural philosophy, and especially to chemistry. In the sixteenth year of his age he joined the Chemical Society of Glasgow, before which he read at least seven papers, including one on *respiration*, another on *fermentation*, and another on *alkalies*. Some of these papers contained suggestions in advance of the science of that day.

While at Glasgow Maclean also studied medicine and anatomy, for it was his purpose to become a surgeon. From Glasgow he went to

Edinburgh, primarily, it may be presumed, to attend the chemical lectures of the celebrated Dr. Joseph Black. From Edinburgh he repaired to London and to Paris, where he had the best facilities for the study of chemistry and surgery. While a student at Paris, Lavoisier, Berthollet and other famous chemists were busy with their investigations, and Maclean was no doubt greatly impressed by them.

After being absent from Glasgow about three years (1787-90), he returned and resumed his studies for another year, and then engaged most successfully in the practice of his profession, continuing at the same time his researches in chemistry. In the twenty-first year of his age he became a member of the Faculty of Physicians and Surgeons of Glasgow University.

Being thoroughly in sympathy with the political sentiments of America, Dr. Maclean left Scotland in April 1795 and arrived at New York the following month. From this city he went to Philadelphia, where he met Dr. Benjamin Rush, a graduate of the class of 1760 of the College of New Jersey and a signer of the Declaration of Independence, who advised him to go to Princeton. Acting upon this suggestion, he formed at Princeton a partnership with Dr. Ebenezer Stockton for the practice of physic and surgery. This partnership was soon dis-

solved, however, for Dr. Maclean was elected to a chair of chemistry in the College of New Jersey and he soon decided to devote his entire time to teaching.

It is of further interest to note that Dr. Maclean came to America the year after Priestley—the same year in which Lavoisier was beheaded. This was before Dalton and Avogadro had propounded their hypotheses, before Gay-Lussac had enunciated the law of gaseous volumes, and before Berzelius introduced modern chemical symbols.

In the early summer of 1795, Dr. Maclean delivered in Nassau Hall a short course of lectures on chemistry, which made a favorable impression. On October 1, 1795, he was elected professor of chemistry and natural history; but the name of the chair was subsequently changed to "mathematics, natural philosophy and chemistry."

In 1797 his salary was £250 per annum; and it was "ordered that chemistry and natural history be taught as branches of natural philosophy." The instruction in these branches was given only to juniors and seniors. Dr. Maclean taught at Princeton until 1812, and for several years his salary was $1,250 a year, together with the use of a college house.

It is of interest to note that chemistry was

taught at some of the older American colleges before laboratories were built and equipped for practical work in chemistry. According to Ernst von Meyer, "the first laboratory in Britain, small though it was, in which a young man had the opportunity of working practically at the subject, was that of Thomas Thomson in Glasgow, established in 1817. This was therefore the first chemical laboratory for general instruction in any country."

Professor Benjamin Silliman, Jr., of Yale, in a paper entitled "American Contributions to Chemistry," which was read July 31, 1874, on the occasion of the Priestley Centennial, said: "Of the public seminaries of learning other than medical institutions where chemistry was taught from a separate chair and as a distinct branch of the college curriculum of instruction prior to 1800, we find but one, and that distinction belongs to Nassau Hall, Princeton, New Jersey."[1]

It should be stated in this connection, however, that James Hutchinson and Dr. James Woodhouse of the University of Pennsylvania, Aaron Dexter of Harvard, and Dr. Samuel Mitchill of Columbia were contemporaries of Maclean, and taught chemistry at a very early period in those institutions.

[1] See *American Chemist* for August and September, 1874, p. 73.—Editor.

There are in the Princeton University library eight letters written by Dr. Maclean at the beginning of the last century, four of which were addressed to Dr. Benjamin Silliman, Sr., who gave his first lecture on chemistry at Yale, April 4, 1804.

The first letter by Dr. Maclean was dated December 1, 1801; it was addressed to the Reverend Dr. Samuel Stanhope Smith, president of the College of New Jersey, and a graduate of the college in the class of 1769. He was a son-in-law of President John Witherspoon, a signer of the Declaration of Independence, whom he succeeded as president of the college. It appears that President Smith had received a letter from President Timothy Dwight, of Yale College, concerning chemical instruction. This was three years before Benjamin Silliman, Sr., began his lectures at Yale. Dr. Maclean's letter is as follows:

My dear Sir:

Be as obliging as to inform Dr. Dwight that I am of the opinion it is impossible for me to require even a slight knowledge of chemistry without either making experiments or seeing them performed, and that to become proficient in the science it will require much practice as well as extensive reading.

The necessity there is for seeing or making experiments proceeds chiefly from the nature of chemistry, but partly also from the manner it has been treated by

those who have written on it. The objects of chemistry are innumerable and very minute, so that no description can be given of even the most simple of its principles which will convey an adequate idea of it to a person who has never seen it performed, and probably it is from being aware of this circumstance that the elementary writers on this science have treated it as if they expected it to be read only by those who were in some degree already acquainted with it and by those who were to have at the same time the assistance of a master.

The books most necessary for a student to have in the profession are . . .

But by far the most valuable part of chemical writings is to be found in the publications of the different learned societies of Europe and in treatises written on particular subjects. The student will find references to most of these in the books above recommended.

The student would do well to furnish himself with a portable chest of chemistry, such as that of Gottling. It contains the most common chemical reagents and is accompanied with a book describing in a plain manner the Chest, and containing directions for performing some simple experiments. It may serve as a very poor substitute for a course of instruction from a master.

I am

Your most obt. servant,

1 Dec., 1801 John Maclean

Rev'd. Dr. Sam. S. Smith.

The next letter was addressed to Benjamin Silliman, under date of August 10, 1803. In this letter Dr. Maclean declined to take boarders, and he gave advice about chemical appara-

tus. This was soon after the burning of Nassau Hall, which occurred on March 6, 1802. It appears that the college professors took students as roomers and boarders after the fire. The most important part of this letter is as follows:

Princeton, 10th Aug., 1803.

Dear Sir:

Your letter of the 6th inst. I received three days ago. The keeping of boarders has never been agreeable to the members of my family. When the College burned we, as well as all the householders in the village, took students into our families; but since it has been rebuilt, we have declined it; so that I have lately been obliged to refuse several applications. . . .

On looking over the list of articles of chemical apparatus in your possession they appear to be sufficient for teaching the principles of chemistry. Perhaps a mercurial pneumatic-chemical trough, a galvanic apparatus, a large double convex lens, and a simple apparatus for the decomposition of water might be added to it with advantage. But there is no end to chemical apparatus. An experimenter will every now and then find that he is in want of something which it was impossible to foresee. However, this is a principle which ought never to be lost sight of, that the more simple an apparatus (provided it be sufficient), the better. A complicated set of machinery, without adding to the accuracy of the experiments, tends to bewilder the student; while a man with plenty of bottles, tubes and corks may, with the assistance of a blowpipe, vary his apparatus so as to perform an infinity of experiments as well for use as amusement.

Our College is doing well. We have 130 students. The buildings we are now erecting are more extensive than was contemplated when I had the pleasure of seeing you. My room—I mean that for philosophical and chemical experiments—will not be finished before January, if then; and the articles necessary to complete my apparatus cannot be here before that time.

Permit me to assure you it will give me much pleasure to see and correspond with you, and believe me

Your most obt. servant,
John Maclean.

Ben. Silliman, Esq.
Yale College,
New Haven.

The third letter was addressed to Silliman when he was a student in Philadelphia. It was in reply to a letter which J. W. Bradford, a Princeton tutor, had received from Silliman. It was written on February 5, 1804, and runs as follows:

Dear Sir:

Mr. Bradford our Tutor has shewn to me your letter of the 27th Jan'y. I am sorry to inform you my dream is yet unfinished and will remain so all winter, so that I am uncertain whether I will attempt to teach Chemistry till the summer; this however will rest with the Faculty. If it be determined that Chemistry is to be taught this winter I will begin in the course of a week and will spend three days each week at it till near the end of our session, which will be on the first Wednesday after the second Tuesday in April. It would give us much pleasure to have you with us at Princeton, and altho' it will be out of my power to try any experiment

of consequence till my room is finished and I get an addition to my apparatus, yet I would be happy to converse with you on the subject of our profession.

I am with much esteem
Your obt. servant,
John Maclean.

N.B. You will oblige me by informing me whether there is any person at Philadelphia who keeps retorts and other chemical vessels for sale as also whether there is any of the red precipitate of mercury—I mean the *pricipitatus per se*—to be had and at what price.

In another letter, dated February 10, 1810, Dr. Maclean congratulated Professor Silliman on his marriage.

The following interesting postscript constitutes a part of this communication: "Have you seen the last number of the *Medical Repository*? If not, be informed that the great Gas Holder Mitchill [Professor of Chemistry, Columbia College], in order to excite a blaze, has thrown two bubbles of hydrogene gas at the heads of the antiphlogistans—God help him; like all other tail bearers of Stahl, he thinks he must be right, if his opponents in any one instance have been wrong. I hope that some one will give him, if he is worthy of notice, that flagellation that he merits."

Benjamin Silliman left in his diary the following statement:[2]

[2] See President Fisher's *Life of Benjamin Silliman, M.D., LL.D.*, Vol. I, pp. 109-10.—Editor.

At this celebrated seat of learning [Princeton], an eminent gentleman, Dr. John Maclean, resided as professor of chemistry, etc. I early attained an introduction to him by correspondence, and he favored me with a list of books for the promotion of my studies. . . . I also passed a few days with Dr. Maclean in my different travels to and from Philadelphia, and obtained from him a general insight into my future occupation; inspected his library and apparatus, and obtained his advice respecting many things. Dr. Maclean was a man of brilliant mind, with all the acuteness of his native Scotland; and a sparkling wit gave variety to his conversation. I regard him as my earliest master in chemistry and Princeton as my starting point in that pursuit; although I had not an opportunity to attend lectures there.

Many years later Dr. Silliman revisited Princeton, and he said to President Maclean upon visiting the chemical laboratory: "It was in this room that I saw the first experiments in chemistry ever witnessed by me."

On the occasion of the Priestley Centennial, Benjamin Silliman, Jr., also said:

Dr. Maclean ever deserves honorable mention as one of the earliest and most successful teachers of our science in this country. . . . In Paris Dr. Maclean learned to admire the antiphlogistic theory, as the "new chemistry" of Lavoisier was called, and which he taught and defended at Princeton. In 1795 he published "Two Lectures on Chemistry, read at Nassau Hall, containing an examination of Dr. Priestley's consideration on the doctrine of phlogiston, and the decomposition of water."

These lectures display both ability and learning and form an interesting chapter in the history of phlogistic discussion.

Dr. Maclean contributed several articles to the New York *Medical Repository*, and his name is associated with that of Professor Silliman in editing the first American edition of Henry's *Chemistry*, in 1808.

The writer recently found in the Library of Princeton University a notebook on chemistry by John Eager Howard, Jr.,[3] of Baltimore, bearing the date of 1806. Howard was a pupil of Dr. Maclean, and his notes are very full and beautifully written. Apparently they are a transcript of Dr. Maclean's lectures. In these notes we find the topics discussed by the lecturer. The following statements are taken from this notebook:

Chemistry enables us to explain many of the changes which this globe undergoes; to comprehend many important phenomena which strike us with wonder and admiration; to invent, improve and bring to perfection many arts and manufactures conducive to our own comfort and happiness; to draw entertainment from the contemplation of appearances which habit has rendered familiar and indifferent to us, and finally by making us more intimately acquainted with the works of the Cre-

[3] John Eager Howard, Jr., was a son of General John Eager Howard, and a grandson of Justice Chew. He graduated at Princeton in 1806 and was at one time a member of Congress.

ator, to enlarge our ideas of his Wisdom, Power and Glory.

Chemistry is the investigation of those intimate and mutual actions of bodies on each other, by which their properties are altered, or their individuality destroyed. . . .

Matter may be divided into dead and living. Of dead substances some are simple and others compound. The simple are those whose composition is unknown, and the compound are such as have been analyzed into simpler parts. The substances which, according to the above definitions, may be considered as simple are:

caloric	silex	fluoric acid	antimony
light	alumine	boracic acid	mercury
electricity	magnesia	arsenic	zinc
oxygene	lime	tungstein	tin
azote	barytes	cobalt	lead
hydrogene	strontites	molybdena	copper
sulphur	pot-ash	bismuth	silver
phosphorus	soda	nickel	gold
carbone	muriatic acid	manganese	platina

There are 37 of these "simple substances," which constitute the titles of so many chapters in the notebook. Seventeen of these were regarded as metals, which were divided into semi-metals (brittle) and metals.

Dr. Maclean also gave a second course in chemistry, which had to do with living or animated bodies. This was a much shorter course, dealing with the structure and organization of vegetables, vegetable products, fixed gross or fat

oils, volatile oils, the composition of vegetables, and tanning and currying.

It thus appears that Dr. Maclean gave attention to the relation of chemistry to agriculture and manufactures as well as to medicine.

The following statement concerning oxygen was written years before its liquefaction: "The term 'gas' expresses a state or form to which bodies are reduced by the operation of caloric. Hence oxygene gas means oxygene in the state of gas. If the gaseous state of a body be owing to its combination with caloric, oxygene has never been found free and uncombined. For oxygene gas retains its form at the lowest temperature with which we are acquainted. It is hence called a permanent gas."

On November 7, 1798, Dr. Maclean was united in marriage to Phebe Bainbridge, eldest daughter of Absalom Bainbridge, practitioner of medicine in New York, and a sister of Commodore William Bainbridge, U.S.A., signalized by the capture of the British frigate *Java* in the war of 1812.

In January 1805, Professor Maclean was chosen a member of the American Philosophical Society.

Dr. Maclean resigned at Princeton in 1812 to accept the chair of chemistry in William and Mary College, Williamsburg, Virginia. He

spent a year at Williamsburg; but, being in poor health, he returned to Princeton at the close of the college year, where he died February 17, 1814, and two days later he was buried in the so-called "Westminster Abbey of America," his grave being contiguous to those of the college presidents and professors, and where all who come and go may read the following inscription on his tomb:

LAUS DEO OPTIMO MAXIMO
Intra hoc Sepulchrum
depositae sunt, spe resurrectionis beatae,
Reliquiae Mortales
Johannis Maclean, M.D.
Viri admodum venerandi:
omnibus dotibus animi praecellentis:
Qui
Glasguae Scotorum natus,
Kal. Martii A.D. MDCCLXXI.
In Americam migravit Anno MDCCXCV.
Physicae Naturalis Scientia penitus instructus,
et
Arte Chemica praecipue florens.
Earum Artium
in Academia Nassovica Professor
designatus est. Prid. Kal. Oct. ejusdem Anni.
Professoribus ac Juventuti in Collegio
Mire dilectus, atque observatus.
E vita eheu decessit,
Omnibus plorandus,
Idibus Februarii
MDCCCXIV

CONSIDERATIONS

ON THE

DOCTRINE

OF

PHLOGISTON,

AND

The Decompoſition of Water.

By JOSEPH PRIESTLEY, *LL. D. F. R. S. &c. &c.*

Qualem commendes etiam atque etiam aſpice. HORACE.

PHILADELPHIA;

PRINTED BY THOMAS DOBSON, AT THE STONE-HOUSE,
N° 41, SOUTH SECOND-STREET.

1796.

To Messrs. Berthollet, De la Place, Monge, Morveau, Fourcroy, and Hassenfratz,

The surviving Answerers of Mr. Kirwan.[1]

Gentlemen,

Having drawn up a short defense of the doctrine of *phlogiston*, I take the liberty of inscribing it to *you*, as the principal advocates for the Antiphlogistic theory. My view in this is to draw your attention once more to the subject, and I request the favour of an answer to my objections. I hope I am not wanting in a proper deference to the opinion of men so justly eminent as yourselves and your friends in France, and also that of great numbers in England, and wherever chemistry is known, who have adopted your hypothesis. But you will agree with me, that no man ought to surrender his own judgment to any mere *authority*, however respectable. Otherwise, your own system would never have been advanced.

As you would not, I am persuaded, have your reign to resemble that of *Robespierre*, few as we are who remain disaffected, we hope you had rather gain us by persuasion, than silence us by power. And though we are all apt to flatter our-

[1] Richard Kirwan (1750-1812), Irish chemist and geologist. He did not abandon the phlogistic theory until 1792.—Editor

selves, we hope we are as willing to be influenced by the former, as we are inflexible to the latter. If you gain as much by your answer to me, as you did by that to Mr. Kirwan, your power will be universally established, and there will be no *Vendée* in your dominions.

Differing as we do in this respect, we all agree in our wishes for the prevalence of *truth*, and also of *peace*, which is wanted as much for the interests of philosophy, as those of humanity. And on this account I earnestly wish success to the arms of France, which has done me the honour to adopt me when I was persecuted and rejected in my native country. With great satisfaction, therefore, I subscribe myself

Your fellow-citizen,

Joseph Priestley.

Northumberland in America,
June 15th, 1796.

CONSIDERATIONS ON THE DOCTRINE OF PHLOGISTON, AND THE DECOMPOSITION OF WATER

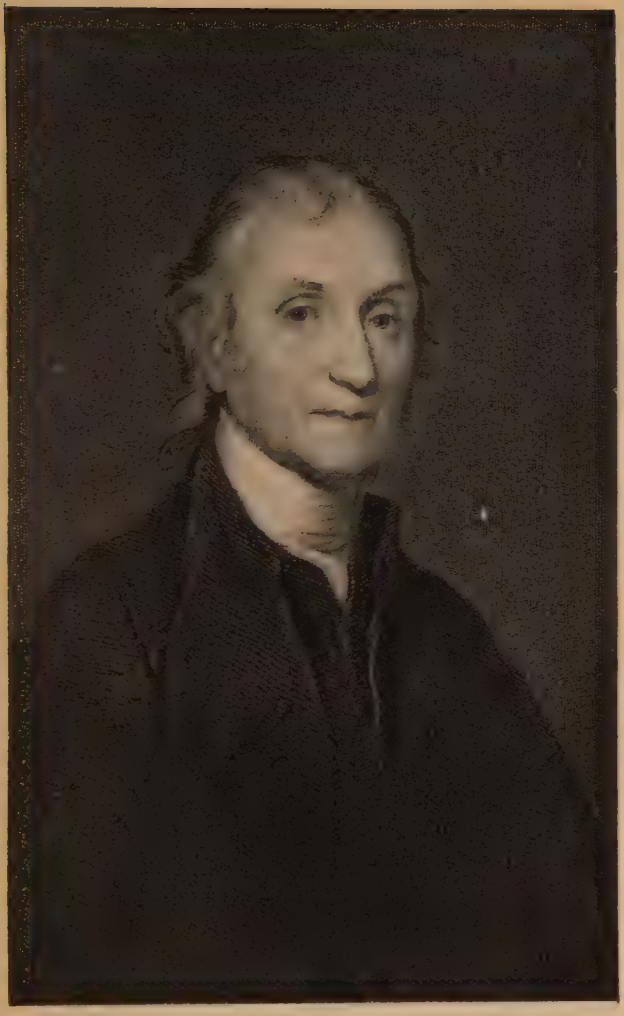
THE INTRODUCTION

THERE have been few, if any, revolutions in science so great, so sudden, and so general, as the prevalence of what is now usually termed *the new system of chemistry*, or that of the *Antiphlogistians*, over the doctrine of Stahl, which was at one time thought to have been the greatest discovery that had ever been made in the science. I remember hearing Mr. Peter Woulfe, whose knowledge of chemistry will not be questioned, say, that there had hardly been any thing that deserved to be called a *discovery* subsequent to it. Though there had been some who occasionally expressed doubts of the existence of such a principle as that of *phlogiston*, nothing had been advanced that could have laid the foundation *of another system* before the labours of Mr. Lavoisier and

his friends, from whom this new system is often called that of the *French*.

This system had hardly been published in France, before the principal philosophers and chemists of England, notwithstanding the rivalship which has long subsisted between the two countries, eagerly adopted it. Dr. Black in Edinburgh, and as far as I hear all the Scots have declared themselves converts and what is more, the same has been done by Mr. Kirwan, who wrote a pretty large treatise in opposition to it. The English reviewers of books, I perceive, universally favour the new doctrine. In America also, I hear of nothing else. It is taught, I believe, in all the schools on this continent, and the old system is entirely exploded. And now that Dr. Crawford is dead, I hardly know of any person, except my friends of the Lunar Society at Birmingham, who adhere to the doctrine of phlogiston; and what may now be the case with *them*, in this age of revolutions, philosophical as well as civil, I will not at this distance answer for.

It is no doubt *time*, and of course opportunity of examination and discussion, that gives stability to any principles. But this new theory has not only kept its ground, but has been constantly and uniformly advancing in reputation, more than *ten years*, which, as the attention of



Joseph Priestley (1733-1804)

so many persons, the best judges of everything relating to the subject has been unremittingly given to it, is no inconsiderable period. Every year of the last twenty or thirty has been of more importance to science, and especially to chemistry, than any ten in the preceding century. So firmly established has this new theory been considered, that a *new nomenclature*, entirely founded upon it, has been invented, and is now almost in universal use; so that, whether [we] adopt the new system or not, we are under the necessity of learning the new language, if we would understand some of the most valuable of modern publications.

In this state of things, an advocate for the old system has but little prospect of obtaining a patient hearing. And yet, not having seen sufficient reason to change my opinion, and knowing that free discussion must always be favourable to the cause of truth, I wish to make one appeal more to the philosophical world on the subject, though I have nothing materially new to advance. For I cannot help thinking that what I have observed in several of my publications has not been duly attended to, or well understood. I shall therefore endeavour to bring into one view what appears to me to be of the greatest weight, avoiding all extraneous and unimportant matter; and perhaps it may be the means

of bringing out something more decisive in point of *fact*, or of *argument*, than has hitherto appeared.

No person acquainted with my philosophical publications can say that I appear to have been particularly attached to any hypothesis, as I have frequently avowed a change of opinion, and have more than once expressed an inclination for the new theory, especially that very important part of it *the decomposition of water*, for which I was an advocate when I published the sixth volume of my experiments; though farther reflection on the subject has led me to revert to the creed of the school in which I was educated, if in this respect I can be said to have been educated in any school. However, whether this new theory shall appear to be well founded or not, the advancing of it will always be considered as having been of great importance in chemistry, from the attention which it has excited, and the many new experiments which it has occasioned, owing to the just celebrity of its patrons and admirers.

SECTION I.

Of the Constitution of Metals

According to the doctrine of phlogiston, advanced by Becher and Stahl in the beginning of

this century, and much simplified and improved since their time, metals, phosphorus, sulphur, and many other substances which are supposed to contain it, are compounds, consisting of this principle, and another which may be called its *base*. Thus each of the metals contains phlogiston united to a peculiar calx, and sulphur and phosphorus consist of the same principle and their respective acid, or the bases of them. But according to the antiphlogistic theory, all the metals are simple substances, and become calces by imbibing pure air; and sulphur and phosphorus are also simple substances, and become the acids of vitriol and of phosphorus by imbibing the same principle, called by them *oxygen*, or the principle, as it probably is, of universal acidity.

As a proof that metals are simple substances, and that they become calces merely by imbibing air, they allege the case of mercury, which becomes the calx called *precipitate per se* by exposure to the atmosphere in a certain degree of heat, and which becomes running mercury again by exposure to a greater degree of heat. They therefore think it impossible not to conclude, that in all other cases of calcination, as well as this, the only difference between the calx and the metal, is that the latter has parted with the air which it had imbibed.

But this is the case of only this particular calx of this metal, and there is another calx of the same metal, viz. that which remains after exposing turbith mineral [basic mercuric sulphate] to a red heat, which cannot be completely revived by any degree of heat, but may be revived in inflammable air, which it imbibes, or when mixed with charcoal, iron-filings, or other substances supposed to contain phlogiston. And if this calx of mercury, or (supposing it to contain some acid of vitriol) this salt, necessarily requires some addition to constitute it a metal, all mercury must contain the same. For though with the same external appearance, the same metal may contain different proportions of any particular principle, as phlogiston, they must be denominated different substances, if some specimens contain this element, and others be wholly destitute of it. All, therefore, that can be inferred from the experiment with the precipitate per se is, that in this particular case, the mercury in becoming that calx imbibed air, without parting with any, or very little, of its phlogiston; and if we judge by the air expelled from the calces of metals and other circumstances, there are few, if any, of them but contain more or less of phlogiston.

I would observe in this place, that it is asserted by some very able chemists, that if the

precipitate per se be made with proper attention, it will be revived without yielding any air. This is also the case with *minium* when fresh made. But this is owing, I doubt not, to their wanting *water*, which I deem to be essential to the constitution of every kind of air; so that they both contain the element of dephlogisticated air, though, for want of water, it is not able to assume that form.

That mercury may have the same external appearance, and all its essential properties, and yet contain different proportions of something that enters into it, is evident from the phenomena of its solution in the nitrous acid, and the revival of its calx in inflammable air. According to the old theory, there is a loss of some part of its phlogiston in the solution of mercury in the nitrous acid, since nitrous air is procured in the process. And though it may be revived from its precipitates by mere heat, yet if it be revived in a vessel of inflammable air, it will imbibe it in great quantities. Mercury revived in these circumstances must contain more phlogiston than that which is revived from the same calx by mere heat. But though mercury revived by mere heat after a solution in nitrous acid must have a deficiency of phlogiston, and when it is revived from precipitate per se in inflammable air must contain a redundancy of the same prin-

ciple, yet there will hardly be a doubt but that, in all chemical processes, it would exhibit the same phenomena.

In all other cases of the calcination of metals in air, which I have called the *phlogistication* of the air, it is not only evident that they gain something, which adds to their weight, but that they likewise part with something. The most simple of these processes is the exposing iron to the heat of a burning lens in confined air, in consequence of which the air is diminished, and the iron becomes a calx. But that there is something emitted from the iron in this process is evident from the strong *smell* which arises from it. If the process be continued, inflammable air will be produced, if there be any moisture at hand to form the basis of it. From this it is at least probable, that, as the process went on in an uniform manner, the same substance, viz. the basis of inflammable air, was continually issuing from it; and this is the substance, or principle, to which we give the name of *phlogiston*.

That the effect of this process is not, as the antiphlogistians assert, the mere separation of the dephlogisticated from the phlogisticated air in that of the atmosphere, I have proved in a course of experiments, in which I have shown that a considerable part of the phlogisticated air that is found after this process is formed in

the course of it, by the union of the phlogiston from the iron with the dephlogisticated air. And if the calcination of the iron in this process be always attended with the loss of some constituent part of it, the same is, no doubt, the case with all other calcinations of the same metal, and also those of all other metals. And farther, if the *metals* be compound substances, containing phlogiston united to some base, the same is the case with *sulphur* and *phosphorus*, because they become acids when they are used in the same process.

According to the antiphlogistic theory, the inflammable air that is produced in the solution of metals in any acid comes wholly from the water combined with it, and not at all from the metal dissolved. But the advocates for this theory do not seem to have attended to one necessary consequence of this supposition. According to their own principles, water consists of eighty-seven parts of oxygen, to only thirteen of hydrogen, in every hundred, which is nearly seven times as much of the former as of the latter. Consequently, since nothing but hydrogen escapes in the process, there must remain, from this decomposition of the water, seven times as much oxygen in the solution. But both Mr. Lavoisier and Mr. de la Place say [*Examination of Mr. Kirwan's Treatise*, p. 197, 198], what

I doubt not is strictly true, that after the process the acid will saturate exactly the same quantity (they do not say more) of alkali, that it would have done before; whereas, with the addition of so much oxygen, it ought to saturate considerably more. If the oxygen from the decomposition of the water do not join that in the acid, what becomes of it?

If this case be analogous to that of the supposed decomposition of water by hot iron, the oxygen ought to be lodged in the iron, and compose finery cinder (magnetic oxide of iron). But this substance is not soluble in vitriolic acid, if that be employed in the experiment; and when it is dissolved in the marine acid, it does not dephlogisticate it, as minium, and other substances containing oxygen, do. It is evident, therefore, that there is no addition of oxygen in this process, consequently no decomposition of water in the case, and that the inflammable air must come from the decomposition of the iron.

SECTION II

Of the Composition and Decomposition of Water

The antiphlogistic theory has received its greatest support from the supposed discovery that water is resolvable into two principles, one

that of *oxygen*, the base of dephlogisticated air, and the other, because it has no other origin than water, *hydrogen*, or that which, with the addition of *calorique*, or the element of *heat*, constitutes inflammable air. "One of the parts of the modern doctrine the most solidly established, say Mr. Berthollet, and the other authors of the *Report* on this subject [*Examination of Kirwan*, p. 17] is the formation, the decomposition, and recomposition, of water. And how can we doubt of it, when we see that, in burning together fifteen grains of inflammable air, and eighty-five of vital air, we obtain exactly an hundred grains of water, in which, by decomposition, we find again the same principles, and in the same proportions. If we doubt of a truth established by experiments so simple, and palpable, there would be nothing certain in natural philosophy. We might even question whether vitriolated tartar be composed of vitriolic acid and fixed alkali, or sal ammoniac of the marine acid and volatile alkali, etc., etc. For the proofs that we have of the composition of these salts are of the same kind, and not more rigorous, than those which establish the composition of water. Nothing perhaps more clearly proves the weakness of the old theory, than the forced explanations that have been attempted to be given of these experiments."

Notwithstanding the confidence thus strongly expressed by these able and experienced chemists, I must take the liberty to say, that the experiments to which they allude appear to me to be very liable to exception, and that the doctrine of phlogiston easily accounts for all that they observed.

Their proof that water is decomposed, and resolved into two kinds of air, is that when steam is made to pass over red-hot iron inflammable air is produced, and the iron acquires an addition of weight, becoming what is called *finery cinder*; but what they call *oxide of iron*, supposing that there is lodged in it the oxygen which was one of the constituent parts of the water expended in the process, while the other part, or the hydrogen, with the addition of heat, assumed the form of inflammable air.

But in order to prove that this addition of weight to the iron is really oxygen, they ought to be able to exhibit it in the form of dephlogisticated air, or of some other substance into which oxygen is allowed to enter, and this they have not done. Iron that has really imbibed air, or the common *rust of iron*, has a very different appearance from this finery cinder, being *red*, and not *black*; and when treated in similar processes, exhibits very different results. Mr. Fourcroy says [*ibid.*, p. 251] that this finery cinder

is "iron partially oxygenated." But if that were the case, it would go on to attract more oxygen, and in time become a proper rust of iron, completely oxygenated. But this is so far from being the case, that finery cinder never will acquire rust; which shows that the iron in this state is saturated with some very different principle, which even excludes that which would have converted it into rust.

However, neither this, nor any other calx of iron, can be revived unless it be heated in inflammable air, which it eagerly imbibes, or in contact with some other substance which has been supposed to contain phlogiston. The probability there is, that the phlogiston then enters this calx of iron, replacing that which had been expelled to form the inflammable air. Nor can any inflammable air be procured in this process with steam, but by means of some substance which has been supposed to contain phlogiston. Where then, is the certain proof that water is decomposed in this process?

It may be said that the oxygen imbibed by this iron, being expelled by heat in contact with inflammable air, unites with that air, and with it constitutes the water which is found after the process. But for any thing that appears, this water may be that which the iron had imbibed,

and which can only be expelled from it by the entrance of that phlogiston which it had lost.

This is the more probable, since, when any other substance which is certainly known to contain oxygen, is heated in the same circumstances, *fixed air* (which is allowed to contain oxygen) is found, and this is not the case with this calx of iron. If, for example, precipitate per se, or minium, be heated in inflammable air, the mercury and the lead will be revived, and a considerable quantity of fixed air will be produced at the same time. But if the air be previously expelled from the minium, which converts it into a yellow substance called *massicot*, though the lead will be revived, no fixed air will be generated. Since, therefore, the result of treating finery cinder and massicot is precisely the same, in the same circumstances, we are fully authorized to conclude that the substances themselves are similar, and consequently that the finery cinder contains no more oxygen than massicot.

In another important respect finery cinder and massicot are similar. They are both soluble in marine acid without dephlogisticating it, which minium instantly does. And yet Mr. Berthollet says, *Annales de Chimie*, Vol. 3, p. 96, that "the heat by which minium becomes massicot cannot change its nature." What is the

evidence of a change in the *nature* of any thing, but a change of its *properties*? On the whole, therefore, the probability is, that when iron is converted into finery cinder, it loses its phlogiston, and imbibes only water; and that when it is reconverted into iron, it parts with the water, and recovers its phlogiston. N.B. The experiment with the massicot must be tried presently after it is made, since it will very soon imbibe air from the atmosphere.

In this place I would observe that, if it be admitted that there is a principle in inflammable air, which, being imbibed by the calx of a metal, converts it into a metallic substance, it will follow that the same principle is contained in charcoal, and other combustible substances; because they will all produce the same effect, and therefore that the principle of inflammability, or phlogiston, is the same in them all.

Another pretended proof that water is composed of dephlogisticated and inflammable air, is that when the latter is burned slowly in the former, they both disappear, and a quantity of water is produced, equal to their weight. I do not, however, find that it was in more than a single experiment that water so produced is said to have been entirely free from acidity, though this experiment was on a large scale, not less than twelve ounces of water being procured.

But the apparatus employed does not appear to me to admit of so much accuracy as the conclusion requires; and there is too much of correction, allowance, and computation, in deducing the result. Also it is, after all, acknowledged that, after decomposing this quantity of the two kinds of air, and making all the allowance they could for the phlogisticated air, or *azote*, in the dephlogisticated air, they found fifty-one cubic inches of this kind of air more than they could well account for. This quantity, therefore, and perhaps something more (since the operators were interested to make it as small as possible) must have been formed in the process. And when this kind of air, as well as inflammable, is decomposed together with dephlogisticated air, nitrous acid is produced. The probability therefore is, that the acidifying principle, or oxygen, in the dephlogisticated air which they decomposed, was contained in that phlogisticated air, and that, had the process been conducted in any other manner, it would have assumed the form of nitrous acid. They acknowledge that, except when the inflammable air was burned *in the slowest manner*, the water they produced had more or less of acidity.

The experiments which I made on the decomposition of these two kinds of air in *close vessels*, appear to me to be much less liable to excep-

tion, and the conclusion drawn from them is the reverse of that of the French philosophers.

When dephlogisticated and inflammable air, in the proportion of a little more than one measure of the former to two of the latter, both so pure as to contain no sensible quantity of phlogisticated air, are inclosed in a glass or copper vessel, and decomposed by taking an electric spark in it, a highly phlogisticated nitrous acid is instantly produced; and the purer the airs are, the stronger is the acid found to be. If phlogisticated air be purposely introduced into this mixture of dephlogisticated and inflammable air, it is not affected by the process, though, when there is a considerable deficiency of inflammable air, the dephlogisticated air, for want of it, will unite with the phlogisticated air, and, as in Mr. Cavendish's experiment, form the same acid. But since both kinds of air, viz. the inflammable and the phlogisticated, contribute to form the same acid, they must contain the same principle, viz. phlogiston.

If there be a redundancy of inflammable air in this process, no acid will be produced, as in the great experiment of the French chemists, but in the place of it there will be a quantity of phlogisticated air. A considerable quantity of *water* is always produced in these decompositions of air. But this circumstance only proves

that the greatest part of the *weight* of all kinds of air is water. I have, in my experiments on *terra ponderosa aerata*[2] demonstrated that water constitutes about half the weight of fixed air.

When the decomposition of dephlogisticated and inflammable air is made in a glass vessel, a peculiarly *dense vapour* is formed, which the eye can easily distinguish not to be mere vapour of *water*, and if the juice of turnsole be put into the vessel, it immediately becomes of a deep red, which shows that it was an acid vapour.

Since the acid that I procured in this process was in considerable quantity, and no phlogisticated air was present (for in the last of my experiments I did not even make use of an air-pump, but first filled the vessel with water, and then displaced it by the mixture of the airs), I do not see how it is possible to account for the formation of this acid but from the union of the two kinds of air; and it can hardly be supposed that, in the very same process, the decomposition of the same substances should compose others so very different from each other as *water* and *spirit of nitre*. I think I have sufficiently accounted for the result of the experiments made by the French chemists on the common hypothesis, which supposes inflammable air to contain phlogiston; but I do not yet see how it is possible

[2] Barium carbonate.—Editor.

for them to explain mine on theirs, according to which there is no such principle in nature. Upon the whole, it does not appear to me that the evidence either for the composition, or the decomposition, of water, is at all satisfactory; and certainly the arguments in support of an hypothesis so extraordinary, and so novel, ought to be of the most conclusive kind.

SECTION III

Other Objections to the Antiphlogistic Theory

Having considered the evidence that has been alleged in support of the antiphlogistic theory, and found it to be insufficient, I shall, in this section, mention a few objections that may be made to it from other considerations.

1. If inflammable air, or hydrogen, be nothing more than a component part of water, it could never be produced but in circumstances in which either water itself, or something into which water is known to enter, is present. But in my experiments on heating finery cinder together with charcoal, inflammable air is produced, though, according to the new theory, no water is concerned. According to this theory, finery cinder, called the *oxide of iron*, consists of nothing besides iron and oxygen; and the charcoal, made with the greatest degree of heat

that can be applied, is equally free from water; and yet when these two substances are mixed together, and exposed to heat, they yield inflammable air in the greatest abundance.

This fact I cannot account for on the principles of the new theory; but nothing is easier on those of the old. For the finery cinder containing water, as one of its component parts, gives it out to any substance from which it can receive phlogiston in return. The water, therefore, from the finery cinder uniting with the charcoal makes the inflammable air, at the same time that part of the phlogiston from the charcoal contributes to revive the iron. Inflammable air of the very same kind is procured when steam is made to pass over red-hot charcoal.

2. Though the new theory discards phlogiston, and in this respect is more simple than the old, it admits another new principle, to which its advocates give the name of *carbone*, which they define to be the same thing with charcoal, free from earth, salts, and all other extraneous substances; and whereas we say that fixed air consists of inflammable air and dephlogisticated air, or oxygen, they say that it consists of this carbone dissolved in dephlogisticated air. [See *Examination of Mr. Kirwan*, p. 79.] Mr. Lavoisier says [*ibid.*, p. 63] that "wherever

fixed air has been obtained, there is charcoal." They therefore call it the *carbonic acid*.

But in many of my experiments large quantities of fixed air have been procured where neither charcoal, nor any thing containing charcoal, was concerned, or none in quantity sufficient to account for it. When the purest malleable iron is heated in dephlogisticated air, or in vitriolic acid air, a considerable quantity of fixed air is formed. It is said that *plumbago* is contained in iron. But it is not found in malleable iron, and least of all in the air that is expelled from it. Fixed air is also produced by reviving minium in inflammable air, and if charcoal of copper be heated in dephlogisticated air, a quantity of fixed air equal to nine-tenths of the dephlogisticated air will be formed. More than thirty ounce measures of the purest fixed air were by this means procured from six grains of this charcoal, which is made by the union of spirit of wine and this metal.

Lastly, fixed air is procured in great abundance in animal respiration. It is true that fixed air is procured by exposing lime-water to atmospherical air, but it is never procured by this means in air confined in any vessel. There must, for this purpose, be an open communication with the atmosphere. But fixed air will be procured in great abundance by breathing air contained

in the smallest receiver, and especially if the air be dephlogisticated. It must therefore be formed by phlogiston, or something emitted from the lungs, uniting with the dephlogisticated air which it meets there. It may be said that since we feed in a great measure upon vegetables (and even animal food is originally formed from them) and this principle of *carbone* is found in all vegetables, *this* may be the substance that is exhaled from the lungs. But since, in this process, it forms the same substance that inflammable air from iron does with dephlogisticated air, or oxygen, it must be the same thing with it; and then this *carbone* will only be another name for *phlogiston*.

3. The antiphlogistians always suppose *azote*, or phlogisticated air, to be a simple substance, though I think abundant evidence has been given (and more will be found in my last memoir, printed in the *Transactions of the Philosophical Society at Philadelphia*), that it is composed of phlogiston and dephlogisticated air.

4. As to the *new nomenclature*, adapted to the new theory, no objection would be made to it, if it were formed, as is pretended, upon a knowledge of the real constitution of natural substances; but we cannot adopt one, the principles of which we conceive not to be sufficiently

ascertained. For other objections to this nomenclature, I refer to the Preface to *Mr. Keir's* excellent *Dictionary of Chemistry*. However, whether we approve of this new language or not, it is now so generally adopted, that we are under a necessity of learning, though not of using it.

On the whole, I cannot help saying, that it appears to me not a little extraordinary, that a theory so new, and of such importance, overturning every thing that was thought to be the best established in chemistry, should rest on so very narrow and precarious a foundation, the experiments adduced in support of it being not only ambiguous, or explicable on either hypothesis, but exceedingly few. I think I have recited them all, and that on which the greatest stress is laid, viz. that of the formation of water from the decomposition of the two kinds of air, has not been sufficiently repeated. Indeed, it requires so difficult and expensive an apparatus, and so many precautions in the use of it, that the frequent repetition of the experiment cannot be expected; and in these circumstances the practiced experimenter cannot help suspecting the accuracy of the result, and consequently the certainty of the conclusion.

But I check myself. It does not become one on a minority, and especially of so small a minority,

to speak or write with confidence; and though I have endeavoured to keep my eyes open, and to be as attentive as I could to every thing that has been done in this business, I may have overlooked some circumstances which have impressed the minds of others, and their sagacity is at least equal to mine.

The phlogistic theory is not without its difficulties. The chief of them is that we are not able to ascertain the *weight* of phlogiston, or indeed that of the oxygenous principle. But neither do any of us pretend to have weighed *light*, or the element of *heat*, though we do not doubt but that they are properly *substances*, capable by their addition, or abstraction, of making great changes in the properties of bodies, and of being transmitted from one substance to another.

N.B. For answers to the objections of Mr. Lavoisier and Mr. Berthollet to some experiments of mine relating to this subject, I refer to the last edition of my *Observations on Air*. Vol. III. p. 554.

TWO LECTURES

ON

COMBUSTION:

SUPPLEMENTARY TO A

COURSE OF LECTURES

ON CHEMISTRY.

READ AT NASSAU-HALL.

CONTAINING

AN EXAMINATION

OF

DR. PRIESTLEY'S CONSIDERATIONS ON THE DOCTRINE OF PHLOGISTON,

AND

THE DECOMPOSITION OF WATER.

BY JOHN MACLEAN,

PROFESSOR OF MATHEMATICS AND NATURAL PHILOSOPHY IN THE COLLEGE OF NEW-JERSEY.

PHILADELPHIA:

PRINTED BY T. DOBSON, AT THE STONE-HOUSE, N° 41, S. SECOND-STREET.

1797.

ADVERTISEMENT

Owing to other engagements, a part only of the first of these lectures was read to the students—They are now printed to save the young gentlemen the trouble of transcribing them.

J. M.

P.S. *It was not till after they were sent to the press, that I was informed Mr. Adet*[1] *had published an answer to Dr. Priestley's pamphlet.*

[1] Pierre Auguste Adet (1763-1832). French envoy to the United States and chemist.—Editor.

Gentlemen,

Although the consequences of the combination of different substances have been explained in the lectures which I have already had the honour of reading to you; yet, as the appearances attending the exposure of inflammable bodies and metals to the air at high temperatures, are peculiarly striking, and have occasioned much disputation among philosophers, it will be proper to consider and compare the different opinions which have been held respecting them.

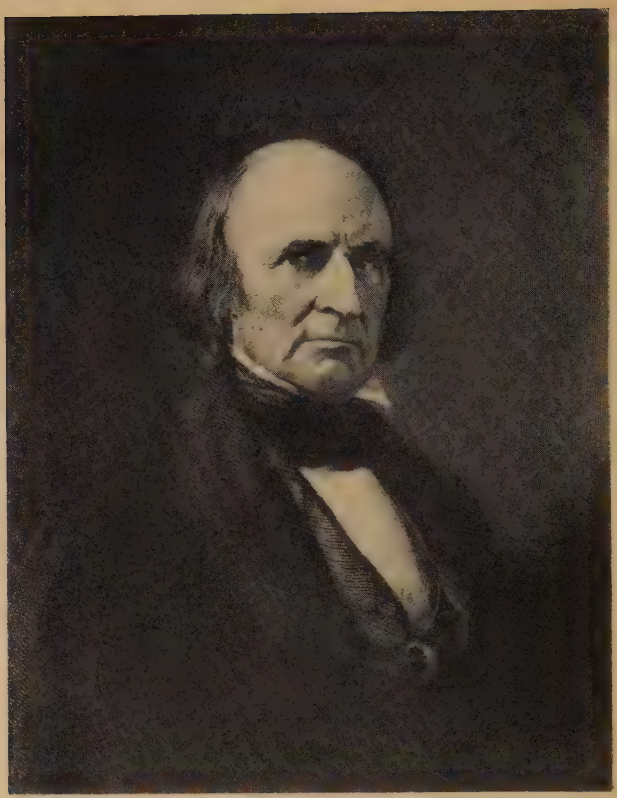
Becher supposed that inflammable bodies contained a substance, which he called inflammable earth.

Stahl thought they included a peculiar principle; to this he gave the name of Phlogiston. He supposed the phenomena of combustion were owing to its escape, and the ashes or residue of a burnt body was matter, by which the phlogiston had been confined. Thus, he thought, that in the combustion of sulphur, the phlogiston was merely separated from the sulphuric acid.

The difference among inflammable bodies, he attributed to the matter containing the phlogiston; and this opinion he considered as confirmed, by the compound of potash and sulphuric acid being readily converted into one of potash and sulphur, by being mixed with powdered charcoal, and raised to a high temperature: for he supposed the charcoal communicated to the sulphuric acid the phlogiston which it had lost.

As all metallic bodies became converted into earthy-like substances when placed in certain circumstances, and as their original properties were restored on their being mixed with inflammable bodies, and raised to a high temperature, Stahl conceived that each metal consisted of phlogiston and a peculiar earth or calx.

It is easy to perceive that Stahl did not attend to the influence the air of the atmosphere has on every ordinary process of combustion. He was ignorant of the composition of the atmosphere: he did not know that one of its parts combines with every inflammable body and metal which is burnt in it; that the new compound is in many cases aërial, or gaseous, and in all exceeds in weight the combustible substance; that this excess of weight corresponds exactly to a like loss sustained by the atmosphere; that in some cases the whole, and in others part, of the substance furnished by the atmosphere, may be separated



Courtesy of the late Edgar Fahs Smith

JOHN MACLEAN (1771-1814)

with all its distinguishing properties; that in every instance the whole of it may be detached by the assistance of other substances, which have a disposition to combine with it; and that in proportion as the separation takes place, the inflammable body, or metal, is recovered. In fine, it may be perceived, that Stahl was unacquainted with many of the phenomena, and formed a conjecture to account for what he had observed.

By the discovery of several of the circumstances just mentioned, Mr. Lavoisier, a celebrated French chemist, was induced to ascribe the change in the properties of inflammable bodies, and metals, by combustion, to their union with the oxygen of the atmosphere, and the great increase of temperature which attends some of these combinations, to the same cause that occasions a like phenomenon, during the combination of other substances.

Mr. Lavoisier was soon supported by several of his countrymen, who were satisfied there was no occasion for supposing the existence of such a principle as phlogiston, to account for the phenomena. Their doctrine has hence been called antiphlogistic.

From its having arisen in consequence of the discovery of several aerial or gaseous substances, it is also named the Pneumatic Doctrine—It is

the system in which you have been instructed.

At first it was strenuously opposed by many philosophers, who, although they admitted Stahl's theory was insufficient, yet thought the existence of phlogiston was not incompatible with the discoveries which had given rise to the antiphlogistic doctrine, and was perhaps even necessary for the explanation of some, if not of all, of the phenomena.

In consequence, many attempts were made to reconcile Stahl's notion with these discoveries; but few phlogistians agreed about the nature of phlogiston. Some of them considered it as an immaterial principle; others thought it was light; others hydrogen gas, etc.; nay, it was not uncommon for the same person to waver between these different opinions.

The event of the contest has been highly honourable to the French chemists. All philosophers now living, except Doctor Priestley, have acceded to their doctrine.

The Doctor has often animadverted on their experiments and conclusions, and being persuaded, that what he has observed has not been properly attended to, or well understood, he has lately published a small pamphlet, entitled, Considerations on the Doctrine of Phlogiston, and the Decomposition of Water. In it he has collected everything he considers as material,

whether as objections to the pneumatic doctrine, or as arguments in favour of that to which he is attached. An examination of these, while it will unfold to you his modification of Stahl's theory, may serve to put you on your guard against falling into even that temporary delusion, which an erroneous opinion is so apt to produce, when supported by a celebrated name.

The work consists of a dedication, an introduction, and three sections: but as the discussion of the subject is confined to the sections, it will be necessary only to consider these.

In the first, he treats of the constitution of metals; in the second, of the decomposition of water; and in the third, of such objections to the pneumatic doctrine as could not conveniently be introduced into either of the other two.

Although this arrangement is not very well suited to our purpose, yet from an anxiety to avoid misrepresentation, I shall retain it; and for the same reason, instead of giving an abridged view of the Doctor's objections and arguments, I shall read his own words; but as he has not adopted the nomenclature in which you have been instructed, I shall mention the names that correspond with those which he employs.

In the section on the constitution of metals, after giving a very brief account of the prin-

ciples of Stahl and Lavoisier, he says, "As a proof that metals are simple substances, and that they become calces (oxyds) merely by imbibing air, they allege the case of mercury, which becomes the calx called precipitate per se (red oxyd of mercury) by exposure to the atmosphere in a certain degree of heat, and which becomes running mercury again by exposure to a greater degree of heat. They therefore think it impossible not to conclude, that in all other cases of calcination, as well as this, the only difference between the calx (oxyd) and the metal, is that the latter has parted with the air which it had imbibed."

This is certainly a very inaccurate statement. The antiphlogistians consider metals as simple, because they have not discovered them to be compound; and they believe the substances, which the Doctor calls calces, are compounds of metals and one part of the air, which they call oxygen, because they cannot be formed without the presence of oxygen; they exceed in weight the metal, and this excess, corresponds to an equal loss of oxygen; and the oxygen may be recovered entirely, in the state of gas, from the red oxyd of mercury, by simply raising its temperature; in part from the red oxyd of lead and black oxyd of manganese by treating them in the same way; and may be wholly separated

from every metallic oxyd, by mixing them with inflammable substances, and raising the temperature of the mixture.

The formation and decomposition of the red oxyd of mercury is ascribed to the oxygen and mercury attracting each other, with different forces, at different temperatures; the partial decomposition of the oxyds of lead and manganese is considered as being owing to these metals retaining different proportions of oxygen with unequal force; and the effect of the inflammable substances is attributed to their having a stronger disposition, than metals have, to combine with oxygen: All which explanations are the more probable, from their corresponding with the laws of chemical combination, discovered by observing the action of different bodies on each other.

After giving the forementioned account of the foundation of the antiphlogistic opinion, the Doctor attempts to show its insufficiency. "But this is the case of only this particular calx (oxyd) of this metal, and there is another calx of the same metal, viz., that which remains after exposing turbith mineral to a red heat, which cannot be completely revived by any degree of heat, but may be revived in inflammable air (hydrogen gas), which it imbibes, or when mixed with charcoal, iron-filings, or other sub-

stances supposed to contain phlogiston. And if this calx of mercury, or (supposing it to contain some acid of vitriol) [sulphuric acid], this salt necessarily requires some addition to constitute it a metal, all mercury must contain the same. For though with the same external appearance, the same metal may contain different proportions of any particular principle, as phlogiston, they must be denominated different substances, if some specimens contain this element and others be wholly destitute of it. All, therefore, that can be inferred from the experiment with the precipitate per se (red oxyd of mercury) is, that in this particular case, the mercury in becoming that calx imbibed air, without parting with any, or very little of its phlogiston; and if we judge by the air expelled from the calces of metals and other circumstances, there are few, if any of them, but contain more or less of phlogiston."

From the following passages in Fourcroy's *Elements of Chemistry*, etc., it appears the reasoning in the paragraph just read is founded on a mistake. Turbith mineral "when urged with a fire in a retort, at first becomes of a deeper colour, and is afterwards reduced to running mercury, giving out at the same time a considerable quantity of vital air (oxygen gas). Kunckel mentions this reduction. It succeeded with

Messrs. Monnet, Bucquet, and Lavoisier, who traced it through all its circumstances. I have repeated it several times with success.

"Perhaps the reason why Mr. Baumé did not obtain running mercury, which has induced him to assert that this yellow oxide does not resume a metallic form unless some combustible substance be added, was his not having applied to it a sufficient heat." [2]

These are confirmed by later observations,[3] and they show, the mercury in turbith mineral, or any substance into which it may be converted by a red heat, does not require any addition to constitute it a metal.

It is true, the presence of hydrogen gas, and other inflammable substances, renders the reduction easier; but this it is contended, only proves, that the substance is decomposed more readily, when there is a body present, which has a disposition to combine with one of its constituent parts, viz., the oxygen, a circumstance analogous to many other chemical decompositions.

The antiphlogistians are induced to believe the hydrogen gas is not imbibed by the mercury, but combines with the oxygen, because, 1*st*. Oxygen gas may be collected, when an oxyd of mercury is reduced by simply raising its tem-

[2] Fourcroy, Vol. II, p. 318. London edition, 1790.

[3] *Annales de Chimie*, Tome X, p. 305.

perature: 2*d*. When the reduction is performed in hydrogen gas this disappears, no oxygen gas is obtained, but a quantity of water may be collected: And, 3*d*. From various experiments it seems, that water is a compound of hydrogen and oxygen.

That a higher temperature is necessary for the decomposition of the substance from turbith mineral, than for that of the red oxyd of mercury, is not at all surprising; they are different bodies, and must therefore be acted on by other agents, with different forces.

The inference, which the Doctor draws from the experiments with the red oxyd of mercury, and from the gas obtained from the oxyds of other metals, cannot be admitted, until he proves the mercury and gas actually contain phlogiston.

The Doctor proceeds—"I would observe in this place, that it is asserted by some very able chemists, that if the precipitate per se (red oxyd of mercury) be made with proper attention, it will be revived without yielding any air. This is also the case with minium (red oxyd of lead) when fresh made. But this is owing, I doubt not, to their wanting *water*, which I deem to be essential to the constitution of every kind of air(gas); so that they both contain the element of dephlogisticated air (oxygen gas), though for

want of water, it is not able to assume that form."

I confess, I am unacquainted with the experiments, which have led to the assertion alluded to in this paragraph.—But, if water be essential to the constitution of every kind of air, and if mercury and lead are converted into their red oxyds, or calces, by uniting with the element of oxygen gas or dephlogisticated air, what precaution can prevent the compounds from imbibing the water, if they have a disposition to do so? The Doctor believes they have such a disposition; for except to these able chemists, they have always afforded oxygen gas or dephlogisticated air, and to do this they must, in his opinion, contain water.

The next paragraph is as follows: "That mercury may have the same external appearance and all its essential properties, and yet contain different proportions of something that enters into it, is evident from the phenomena of its solution in the nitrous acid, and the revival of its calx in inflammable air (hydrogen gas). According to the old theory, there is a loss of some part of its phlogiston in the solution of mercury in the nitrous acid, since nitrous air (gas) is procured in the process: And though it may be revived from its precipitates (oxyds) by mere heat, yet if it be revived in a vessel of inflam-

mable air (hydrogen gas), it will imbibe it in great quantities. Mercury revived in these circumstances must contain more phlogiston than that which is revived from the same calx by mere heat. But though mercury revived by mere heat after a solution in nitrous acid must have a deficiency of phlogiston, and when it is revived from precipitate per se (red oxyd of mercury) in inflammable air (hydrogen gas) must contain a redundancy of the same principle, yet there will hardly be a doubt but that, in all chemical processes, it would exhibit the same phenomena."

If two portions of matter exhibit the same phenomena in all chemical operations, they ought most certainly to be considered as the same substance; and as mercury revived from its oxyds by a mere increase of temperature, possesses all the properties of that revived by the assistance of hydrogen gas, etc., it cannot be in any respect deficient. It is in vain to say, that it must be so, because "according to the old theory, there is a loss of some part of its phlogiston in the solution of mercury in the nitrous acid," and if it be revived in hydrogen gas "it will imbibe it in great quantities"; it is first incumbent to prove, that the old theory, as he calls it, is right, and that the gas which disappears, is

actually absorbed by the mercury: but these are just the subjects of dispute.

Having said so much on mercury he observes, "In all other cases of the calcination (oxydation) of metals in air, which I have called the phlogistication of the air, it is not only evident that they gain something which adds to their weight, but that they likewise part with something. The most simple of these processes is the exposing iron to the heat of a burning lens in confined air, in consequence of which the air is diminished and the iron becomes a calx (oxyd). But that there is something emitted from the air in this process is evident from the strong smell which arises from it. If the process be continued, inflammable air (hydrogen gas) will be produced, if there be any moisture at hand to form the basis of it. From this it is at least probable, that, as the process went on in an uniform manner, the same substance, viz., the basis of inflammable air (hydrogen gas), was continually issuing from it; and this is the substance, or principle, to which we give the name of phlogiston."

"That the effect of this process is not, as the antiphlogistians assert, the mere separation of the dephlogisticated from the phlogisticated air (the oxygen from the azotic gas) in that of the atmosphere, I have proved in a course of ex-

periments, in which I have shown that a considerable part of the phlogisticated air (azotic gas) that is found after this process, is formed in the course of it, by the union of the phlogiston from the iron with the dephlogisticated air (oxygen gas). And if the calcination of the iron in this process be always attended with the loss of some constituent part of it, the same is, no doubt, the case with all other calcinations of the same metal, and also those of all other metals. And further, if the metals be compound substances, containing phlogiston united to some base, the same is the case with *sulphur* and *phosphorus*, because they become acids when they are used in the same process."

I do not know, that a smell arises from pure iron when heated in air: but most certainly there are other metals, from which no smell arises, when placed in the same circumstances; and the Doctor has said, if the calcination of iron be attended with the loss of some constituent part of it, meaning phlogiston, the same is no doubt the case with those of all other metals; and therefore even although iron should afford a smell, it is no proof of the escape of phlogiston.

That a quantity of hydrogen gas is obtained when the air or iron is moist is most certain: but this, it is insisted, is owing to the iron uniting

with the oxygen of the water, while the hydrogen assumes the form of gas or air.

I have not been able to find any course of experiments, which *proves*, that azotic gas is formed by exposing iron in confined air to the rays of the sun concentrated by a burning lens: but Dr. Priestley informs us, that on examining the residuum of some "pretty pure dephlogisticated air (oxygen gas)" in which iron had been fired with assistance of a lens, "it did not appear that any phlogisticated air (azotic gas) had been produced in the process,"[4] and the same thing has been observed by Lavoisier,[5] consequently azotic gas cannot be formed by any thing from the iron uniting with oxygen, and the argument for the existence of phlogiston drawn from its supposed formation is invalid.

From the effects of air at high temperatures, the Doctor passes to those of acids on metals. "According to the antiphlogistic theory, the inflammable air (hydrogen gas) that is produced in the solution of metals in any acid, comes wholly from the water combined with it; and not at all from the metal dissolved. But the advocates for this theory do not seem to have

[4] *Experiments and Observations on Air*, Vol. III, p. 481.

[5] Il est de même extrêmement difficile d'obtenir du gaz oxigine parfaitement pur, il contient presque toujours une petite portion de gas azote, mais elle ne trouble en rien le résultat de l'expérience, & elle se retrouve à la fin en même quantité qu'au commencement. *Annales de Chimie*, Tome I, p. 26.

attended to one necessary consequence of this supposition. According to their own principles, water consists of eighty seven parts of oxygen, to only thirteen of hydrogen in every hundred, which is nearly seven times as much of the former as of the latter. Consequently since nothing but hydrogen escapes in the process, there must remain, from this decomposition of the water, seven times as much oxygen in the solution. But both Mr. Lavoisier and Mr. de la Place say [Examination of Mr. Kirwan's Treatise, p. 197, 198] what I doubt not is strictly true, that after the process the acid will saturate exactly the same quantity (they do not say more) of alkali, that it would have done before; whereas, with the addition of so much oxygen, it ought to saturate considerably more. If the oxygen from the decomposition of the water do not join that in the acid, what becomes of it?"

The answer to this question is very easy—Far from supposing the oxygen from the water joins that in the acid, the antiphlogistians believe it unites with the metal, to enable this to combine with the acid. They are of this belief, because the metal is precipitated in a state of oxyd when an alkali is added to the solution; while the acid requires the same quantity of alkali to saturate it, and forms the same substances that it would have done before its action on the metal.

Perhaps it was from being aware of this answer that the Doctor has said, in the next paragraph, which concludes the section, "If this case be analogous to that of the supposed decomposition of water by hot iron, the oxygen ought to be lodged in the iron, and compose *finery cinder* (black oxyd of iron). But this substance is not soluble in vitriolic (sulphuric) acid, if that be employed in the experiment; and when it is dissolved in the marine (muriatic acid), it does not dephlogisticate (oxygenate) it, as minium (red oxyd of lead) and other substances containing oxygen, etc. It is evident, therefore, that there is no addition of oxygen in this process, consequently no decomposition of water in the case, and that the inflammable air (hydrogen gas) must come from the decomposition of the iron."

It is rather surprising the Doctor should assert, that finery cinder (black oxyd of iron) is not soluble in sulphuric acid, when in page 505 of the third volume of his own experiments and observations, it is said, that of sixty grains of finery cinder put into vitriolic (sulphuric) acid,[6] fifteen grains remained undissolved. Besides, there is the most satisfactory evidence that iron, after its solution in the sulphuric acid, is in a state like that of the black oxyd or finery cinder. This substance dissolves in the acid without

[6] The quantity of acid is not specified.

effervescence,[7] and if the precipitate which the solution of iron in the sulphuric acid affords, on the addition of an alkali, be collected as soon as it falls, and dried in close vessels, it will be the black oxyd.[8] There is no effervescence during the solution, because there is no hydrogen gas evolved; and this, the antiphlogisticians believe, is owing to the iron being previously combined with enough of oxygen to supersede the necessity of decomposing the water. The precipitate must be dried immediately, and in close vessels, because, from the minute division, it is very liable to be oxydated to a greater degree.

The other circumstance which he has adduced as a proof, that the black oxyd does not contain oxygen, is not more convincing. It certainly does not follow, because muriatic acid can separate a certain portion of oxygen from lead, when this is combined with a great quantity of that substance, that it should likewise separate oxygen from iron, when this is united to a comparatively small quantity.

From this first section of the Doctor's work it seems, his objections to the opinion, that metals are simple, and become converted into earthy-like bodies by an union with oxygen, are, 1*st*. The substance which remains after exposing

[7] Lavoisier's *Elements of Chemistry*, p. 88. Edinburgh Edition, 1790.

[8] Fourcroy, Vol. II, p. 425.

turbith mineral to a red heat, cannot be made to yield its mercury unless it be mixed with bodies supposed to contain phlogiston. 2*d*. When iron is fired in air it emits a smell, and if there be moisture at hand, inflammable air (hydrogen gas) is produced. 3*d*. Phlogisticated air (azotic gas) is formed during the combustion of iron. 4*th*. If oxygen was separated from hydrogen during the solution of iron in acids, these should acquire a proportional addition of strength. And, 5*th*. Iron dissolved in the sulphuric acid is not in the state of the black oxyd.

It also appears that the Doctor is of opinion,

1. That metals contain phlogiston.

2. That, in the formation of precipitate per se (red oxyd of mercury), air is absorbed, and little or no phlogiston emitted.

3. That mercury revived from its calces (oxyds) by mere heat contains less phlogiston than when revived with the assistance of inflammable air (hydrogen gas).

4. That the smell which arises from heated iron, is owing to the phlogiston which is escaping, and that the inflammable air (hydrogen gas) which is produced when moisture is at hand, is formed by the union of the phlogiston with the water.

5. That phlogisticated air (azotic gas) is

formed by the union of phlogiston with dephlogisticated air (oxygen gas).

6. That the inflammable air (hydrogen gas) emitted during the solution of iron in acids, is owing to the decomposition of the iron. And,

7. That *finery cinder* (black oxyd of iron) does not contain oxygen.

But from the facts mentioned in the review of the section it follows, 1. The substance into which turbith mineral may be converted by a red heat, affords its mercury by a simple increase of temperature.

2. Mercury, revived from its oxyds by a simple increase of temperature, does not differ from that revived in hydrogen gas.

3. If a smell arises from heated iron, it is no proof of the emission of phlogiston.

4. Azotic gas cannot be formed by the union of oxygen with anything emitted from heated iron.

And, 5. Iron, when dissolved in sulphuric acid, is reduced to a state like that of the black oxyd.

And further, if it can be proved that water is a compound of hydrogen and oxygen, and susceptible of decomposition, as is insisted by the antiphlogistians, it must also follow, that hydrogen gas, and other inflammable substances, assist the reduction of metallic oxyds, by com-

bining with their oxygen. And that the hydrogen gas obtained by exposing heated iron to moisture, or by dissolving iron in diluted sulphuric acid, proceeds from the decomposition of the water, and not from that of the iron.—But the proofs of these will be exhibited in the examination of the second section.

The second section of Dr. Priestley's work is the most important. He begins it with observing, "The antiphlogistic theory has received its greatest support from the supposed discovery, that water is resolvable into two principles: one that of oxygen, the base of dephlogisticated air, and the other, because it has no other origin than water, hydrogen, or that which, with the addition of calorique, or the element of heat, constitutes inflammable air."

The term hydrogen is derived from ὕδωρ, aqua, and γείνομαι, gignor, and was designed to express the principle engendering water. It has been criticised by some, who maintain it signifies, engendered by water, and this is the sense in which Dr. Priestley seems inclined to understand it. But, as has been well observed by Mr. Lavoisier, it may be used in either of these acceptations; for where water is decomposed hydrogen is produced, and when hydrogen is combined with oxygen water is produced.

After giving an abstract from a joint work

by several of the antiphlogistians, in which they declare their firm belief in the formation, the decomposition, and recomposition of water, the Doctor says,

"Notwithstanding the confidence thus strongly expressed by these able and experienced chemists, I must take the liberty to say, that the experiments to which they allude appear to me to be very liable to exception, and that the doctrine of phlogiston easily accounts for all that they observed.

"Their proof that water is decomposed, and resolved into two kinds of air, is, that when steam is made to pass over red-hot iron inflammable air is produced, and the iron acquires an addition of weight, becoming what is called finery cinder; but what they call oxide of iron, supposing that there is lodged in it the oxygen which was one of the constituent parts of the water expended in the process, while the other part, or the hydrogen, with the addition of heat, assumed the form of inflammable air."

It ought to have been stated, that in this experiment there is a loss of water exactly equal to the joint weight of the addition made to the iron, and of the hydrogen gas obtained.

The antiphlogistians suppose the addition made to the iron to be oxygen, because the compound resembles, in every respect, as the Doc-

tor himself allows, that substance which is formed by burning iron in oxygen gas, or in atmospherical air; and this they consider as an oxyd, because, 1*st*. While it is forming the oxygen gas disappears, and its weight is exactly equal to that of the iron, and the oxygen consumed:[9]—And, 2*d*. When iron-filings are mixed with red oxyd of mercury, and the mixture made nearly red-hot, the iron is converted into the same black substance as in the last experiment, while the oxyd of mercury is reduced, and the weight acquired by the iron corresponds to the excess of that of the red oxyd above the mercury.[10]

The hydrogen gas is supposed to come from the water, and not from the iron, because it is

[9] Quand on a donné à cette expérience toute l'attention qu'elle mérite, l'air se trouve diminué d'une quantité en poids exactement égale à celle dont le fer est augmenté. *Annales de Chimie*, Tome I, p. 24.

[10] J'ai mêlé ensemble [says Mr. Lavoisier], 450 grains d'oxide rouge de mercure, par le feu, bien pur, & 100 grains de limaille d'un fer tres doux, et qui n'etoit nullement attaqué de rouille. J'ai introduit ce mêlange dans une petite cornue, & j'ai fait chauffer jusqu'au moment seulment où les vaisseaux ont commencé obscurément à rougir. Il ne s'est dégagé aucun gaz pendant cette operation, si ce n'est une tres médiocre quantité d'air fixe ou acide carbonique aériforme; elle n'excédoit pas deux ou trois pouces cubiques. Il a passé dans la distillation 415 grains de mercure coulant; ayant ensuite cassé la cornue, j'ai trouvé la limaille de fer dans l'état d'un fer brûlé, elle étoit friable, elle se réduisoit aisément en poudre, elle étoit dans l'état d'un véritable *éthiops* (black oxyd) & pesoit 132 grains. *Annales de Chimie*, Tome I, p. 28.

not obtained when the black oxyd is formed, without the assistance of water; and, as will be shown, water may be formed by uniting oxygen with hydrogen.

The Doctor observes, on the experiment with iron and water, "But in order to prove that this addition of weight to the iron is really oxygen, they ought to be able to exhibit it in the form of dephlogisticated air (oxygen gas) or some other substance into which oxygen is allowed to enter and this they have not done. Iron that has really imbibed air, or the common *rust of iron*, has a very different appearance from this finery cinder (black oxyd of iron) being red, and not black; and when treated in similar processes, exhibits very different results. Mr. Fourcroy says [Examination of Kirwan, p. 251] that this finery cinder is 'iron partially oxygenated.' But if that were the case, it would go on to attract more oxygen, and in time become a proper rust of iron, completely oxygenated. But this is so far from being the case, that finery cinder never will acquire rust; which shows, that the iron in this state is saturated with some very different principle, which even excludes that which would have converted it into rust."

The evidence which has been given, seems to me to be sufficient to prove the addition made

to the iron must be oxygen; but more will be given in the course of these lectures.

Without doubt common rust of iron is very different from the black oxyd; but the Doctor is certainly mistaken in supposing this cannot acquire rust; Mr. Fourcroy says, it rusts sooner than common iron, and every apothecary knows it does so. Besides, we learn from the experiments of Messrs. Joffe and Fourcroy, that if rust be made red hot in a retort, a quantity of carbonic acid is disengaged from it, and the iron remains in the state of black oxyd. The rust therefore is a carbonate of iron, and must contain all the principles which compose the black oxyd; and this can contain none capable of excluding that which would convert it into rust.

The Doctor then remarks, "However, neither this, nor any other calx of iron, can be revived, unless it be heated in inflammable air (hydrogen gas), which it eagerly imbibes, or in contact with some other substance which has been supposed to contain phlogiston. The probability therefore is, that the phlogiston then enters this calx of iron, replacing that which had been expelled to form the inflammable air. Nor can any inflammable air be procured in this process with steam, but by means of some substance which has been supposed to contain phlogiston.

Where then is the certain proof that water is decomposed in this process?"

The supposition that a body contains phlogiston is no proof that it does so.

"It may be said, that the oxygen imbibed by this iron, being expelled by heat in contact with inflammable air (hydrogen gas), unites with that air, and with it constitutes the water found after the process. But for any thing that appears, this water may be that which the iron had imbibed, and which can only be expelled from it by the entrance of that phlogiston which it had lost."

Doubtless you will be surprised to hear, that water is the substance which the Doctor supposes is capable, when combined with iron, of excluding that which would convert it into rust; and you will recollect that black oxyd of iron can be formed without the assistance of water.

It is true, the Doctor observes on the formation of the black oxyd in oxygen gas and atmospherical air, that "by far the greatest part of the weight of dephlogisticated air (oxygen gas) is water, and the air being decomposed in the process, the water is imbibed by the iron, and the acidifying principle (oxygen) contributes to form," according to the publication now under review, phlogisticated air (azotic gas) but by his experiments and observations, "fixed air

(carbonic acid gas),[11] with the phlogiston which is at the same time expelled from the iron."[12]

It has been already shown, that no azotic gas is formed by the combustion of iron in oxygen gas; and the quantity of carbonic acid which has been found in the remainder of oxygen gas, in which iron has been burned, is very trifling, and is owing partly to the gas containing some before the operation, and partly to plumbago contained in the iron.[13]

But moreover, if the Doctor's explanation of the formation of the carbonic acid gas be accurately examined, it will be found inconsistent with many of his own principles.

He believes water is a constituent part of oxygen gas, because, from certain experiments, he has inferred it constitutes one half of carbonic acid gas, and enters into the composition of all aerial fluids: and from the quantity of water obtained on burning hydrogen in oxygen gas, he supposes it constitutes nine parts in ten of oxygen gas.[14]

It will be shown in the next lecture, that his opinion respecting the composition of gases is not well founded; but for the sake of argument, let it for the present be granted, that oxygen

[11] See p. 15.
[12] *Experiments and Observations*, Vol. III, p. 551.
[13] *Annales de Chimie*, Tome III, pp. 91-97.
[14] *Experiments and Observations*, Vol. III, p. 535.

gas is compounded as he supposes, and that carbonic acid gas consists "of about one half water, and the other phlogiston and dephlogisticated air[15] (oxygen gas) in the proportion of one fourth of the former, to three fourths of the latter."

In page 159 of the first volume of his Experiments and Observations, he says, "In six ounce measures and a half of dephlogisticated air (oxygen gas), I melted turnings of malleable iron till there remained only an ounce measure and one third; and of this twenty-seven thirtieths of an ounce measure was fixed air (carbonic acid gas)." Consequently the oxygen gas concerned in the formation of the carbonic gas, must have occupied the space of 6.06 ounce measures.[16]

An ounce measure is equal to 1.8980 cubic inch, and therefore 6.06 ounce measures are equal to 11.501 cubic inches.

A cubic inch of oxygen gas weighs .34211 of a grain;[17] and 11.501 cubic inches weigh 3.9346 grains.

The weight of a cubic inch of carbonic acid

[15] He means what he calls the acidifying principle or oxygen.

[16] The volume of gas that disappeared was 5.16 ounce measures, and that of the carbonic acid was 0.9 of an ounce measure.

[17] Lavoisier's *Elements*, Edinburgh Edition. Appendix, p. 490.

gas is .44108 of a grain;[18] and that of .9 of an ounce measure, or 1.7082 cubic inch, is .75345 of a grain.

The 3.9346 grains of oxygen gas, consumed in the experiment, consisted, according to the Doctor's estimation, of 3.54114 grains of water, and .39346 of a grain of oxygen: and the .75345 of a grain of carbonic acid gas consisted of .37672 of a grain of water, .09418 of a grain of phlogiston, and .28254 of a grain of oxygen. Therefore the oxygen admitted into the carbonic acid gas was less than that contained in the oxygen gas. What became of the rest?[19]

But the insufficiency of the Doctor's account of the formation of the carbonic acid gas will more clearly appear, on comparing the combustion of iron with that of charcoal.

"I heated (says he)[20] eight grains and a quarter of perfect charcoal, in 70 ounce measures of dephlogisticated air (oxygen gas) of the standard of 0.46, when it still continued 70 ounce measures; but after washing in water, it was reduced to 40 ounce measures of the standard of 0.6, and the charcoal then weighed a grain

[18] *Ibid.*

[19] The above calculation is made on the supposition that all the carbonic acid was formed during the process, although it is probable some of it was contained in the oxygen gas before the combustion of the iron.

[20] *Experiments and Observations*, Vol. III, p. 377.

and a quarter." Supposing this experiment to have been accurate, which is not easy to do, the quantity of oxygen gas consumed was 19.47974 grains, and that of the carbonic acid obtained was 25.11509 grains. According to the Doctor, the first consisted of 1.947974 grains of oxygen, and 17.531766 grains of water; and the second of 9.418159 grains of oxygen, 3.139386 grains of phlogiston, and 12.557545 grains of water.

By this statement, the carbonic acid gas did not contain so much water as the oxygen gas; yet there is none of that fluid deposited when perfect charcoal is burnt in dry oxygen gas: the phlogiston in the carbonic acid was not half the weight of the consumed charcoal; although the Doctor says, page 166, Vol. I of his Experiments and Observations, that charcoal is very nearly pure phlogiston; the oxygen in the carbonic acid gas was almost five times as much as that in the oxygen gas; and from the experiment with iron, the oxygen in the oxygen gas ought to have formed 3.73023 grains of carbonic acid gas, whereas the quantity said to have been obtained was 25.11509 grains.

It is plain, therefore, the formation of the carbonic acid gas cannot be accounted for, by supposing the two gases to be compounded in the manner alleged by the Doctor, and charcoal to be pure phlogiston.

But he has said in page 547 of the third Volume "that charcoal contains all the element of fixed air (carbonic acid gas), the acidifying principle as well as phlogiston."—However, even this supposition will not be sufficient to remove the difficulty.

It has been already mentioned, that of the 25.11509 grains of carbonic acid gas, 3.73023 grains should on the Doctor's principles be formed by the assistance of the oxygen gas; the phlogiston supposed by him to be necessary for this quantity is equal to .46627 of a grain, and ought to have been furnished by the charcoal. The remainder of the seven grains of charcoal should have consisted of phlogiston and oxygen, in a proportion fit for making, on the addition of water, the carbonic acid gas. But the remainder is 6.53373 grains; and as water is supposed to constitute one half of the carbonic acid gas, it ought to have formed 13.06746 grains, and these with the 3.73023 grains are less than the quantity said to have been formed by 8.31740 grains.

Now, as the formation of the carbonic acid gas by the combustion of charcoal cannot be reconciled to the supposed composition of the two gases, and as the explanation which the Doctor has given, of the formation of the same gas by the combustion of iron is founded on the

same principles, it cannot possibly be just. And further, as his opinion of the composition of finery cinder rests on the propriety of the explanation which he has given of the formation of the azotic gas, or of that of the carbonic acid gas, and as both have been shown to be wrong, it also must be groundless.

In confirmation of his opinion the Doctor proceeds: "This is the more probable, since when any other substance, which is certainly known to contain oxygen, is heated in the same circumstances, fixed air (carbonic acid, which is allowed to contain oxygen) is found, and this is not the case with the calx of iron. If for example precipitate per se, or minium (the red oxyds of mercury and lead) be heated in inflammable air, the mercury and the lead will be revived, and a considerable quantity of fixed air (carbonic acid gas) will be produced at the same time. But if the air be previously expelled from the minium which converts it into a yellow substance called massicot (yellow oxyd of lead) though the lead will be revived, no fixed air (carbonic acid gas) will be generated. Since therefore, the result of treating finery cinder (black oxyd of iron) and massicot is precisely the same, in the same circumstances, we are fully authorized to conclude that the substances themselves are similar, and consequently

that the finery cinder contains no more oxygen than massicot."

Together with some water, a small but not a considerable quantity of carbonic acid gas is commonly obtained, when the red oxyds of mercury and lead are revived in hydrogen gas. In one experiment made with red oxyd of mercury, sent to the Doctor by Mr. Berthollet, he obtained 0.04 of an ounce measure of carbonic acid gas; and in another, made with red oxyd of lead, he procured 0.028 of an ounce measure.[21]

Metallic oxyds are much disposed to unite with carbonic acid, and therefore the small quantity obtained in the above instances, might with safety be attributed, to their having attracted it from the atmosphere and parted with it during the reduction.

But Mr. Berthollet informs us,[22] the oxyd which he gave to the Doctor actually did contain carbonic acid: On distilling 50 grains of it and receiving the gas over lime water, although this was not at first made turbid, after about a quarter of an hour it deposited a considerable precipitate. The precipitate he ascribed to carbonic acid uniting with the lime; and its slow formation to the acid being held in solution by a great quantity of oxygen gas, and to the portions

[21] *Experiments and Observations*, Vol. I, p. 168.

[22] *Annales de Chimie*, Tome III, p. 91.

of the carbonate of lime which were first formed being dissolved by the unchanged lime water.

Dr. Priestley observes on this experiment of Mr. Berthollet, "The precipitate per se with which Mr. Berthollet furnished me, he says, contained a considerable quantity of fixed air; and yet he allows that when admitted to lime water, it did not immediately make it turbid, which it is well known a tenth part of the fixed air which I procured would have made it instantly and completely white. The turbulency that came on afterwards must therefore have had some other cause, probably some acid of vitriol (sulphuric acid) in the water of the trough in which the experiment was made, and which gradually insinuating itself into the lime water in his tube, would make *a selenite* (sulphate of lime), a thing that has frequently occurred in the course of my own experiments, and which for some time puzzled me not a little."[23]

But although the carbonic acid gas which he obtained would make a certain quantity of lime water instantly turbid, it is not well known that it would do so when combined with seven or eight cubical inches of oxygen gas. Mr. Berthollet does not say that the water in the trough of his pneumato-chemical apparatus was different from that in the vessel in which he re-

[23] *Experiments and Observations*, Vol. III, p. 559.

ceived the oxygen gas; and I cannot believe a man of his accuracy would think of filling the trough, for such an experiment, with any other than lime water.

The yellow oxyd of lead may be formed by making the red oxyd red hot, or by exposing lead to the same temperature and in contact with air. It affords no carbonic acid gas when it is reduced in hydrogen gas, not from its being destitute of oxygen, but from its containing no carbonic acid. The temperature to which it has been previously submitted is unfavorable to its union with carbonic acid; but if when cooled, it be exposed for a short time to the air, it will imbibe that substance and yield it when reduced in hydrogen gas.

It will be readily allowed by the antiphlogistians, that if yellow oxyd of lead does not contain oxygen, the black oxyd of iron does not do so either: but the yellow oxyd cannot be made without the presence of oxygen gas or atmospherical air; it is heavier than the lead in its composition; and its not affording carbonic acid is no proof that it does not contain oxygen.

The Doctor observes further in support of his opinion, "In another important respect finery cinder (black oxyd of iron) and massicot are similar. They are both soluble in marine (muriatic) acid without dephlogisticating (oxygenat-

ing) it, which minium (red oxyd of lead) instantly does. And yet Mr. Berthollet says [*Annales de Chimie*, Vol. III, p. 96] that 'the heat by which minium becomes massicot cannot change its nature.' What is the evidence of a change in the nature of any thing, but a change of its properties? On the whole, therefore, the probability is, that when iron is converted into finery cinder, it loses its phlogiston, and imbibes only water; and that when it is reconverted into iron, it parts with the water, and recovers its phlogiston. N.B. the experiment with the massicot must be tried presently after it is made, since it will very soon imbibe air from the atmosphere."

The red contains more oxygen than the yellow oxyd of lead. Its parting with some oxygen to the muriatic acid is only a proof of what has been already noticed, that the lead retains different quantities of oxygen with unequal force.

The quotation from Mr. Berthollet is not exact. It is his intention to express, that the carbonic acid and azote, with which red oxyd of lead is commonly contaminated, may be separated by a high temperature, and yet the lead remain in the state of an oxyd.

The reason why the experiment with massicot must be tried presently after it is made has been already assigned.

Now, considering the manner in which the finery cinder and massicot are formed, and that the different circumstances which have been alleged as proofs of their not containing oxygen are incompetent, the probability is, that they do not consist of water, and iron, and lead, deprived of phlogiston.

The Doctor then says, "In this place I would observe that, if it be admitted that there is a principle in inflammable air (hydrogen gas), which, being imbibed by the calx of a metal, converts it into a metallic substance, it will follow that the same principle is contained in charcoal, and other combustible substances; because they will all produce the same effect, and therefore that the principle of inflammability, or phlogiston, is the same in them all."

This will readily be admitted, but by the same mode of reasoning it must follow, that if a substance causes the reduction of a metallic oxyd without communicating any thing to it, there can be no occasion for the addition of any principle, and consequently no such principle as phlogiston existing.

From the decomposition, the Doctor passes to the recomposition of water: but the consideration of his observations on this subject must be deferred to the next lecture.

Dr. Priestley is as much dissatisfied with the proofs of the recomposition, as with those of the decomposition of water. "Another pretended proof [says he] that water is composed of dephlogisticated and inflammable air (oxygen and hydrogen gases), is that when the latter is burned slowly in the former, they both disappear, and a quantity of water is produced, equal to their weight. I do not, however, find that it was in more than a single experiment that water so produced is said to have been entirely free from acidity, though this experiment was on a large scale, not less than twelve ounces of water being procured. But the apparatus employed does not appear to me to admit of so much accuracy as the conclusion requires; and there is too much of correction, allowance, and computation, in deducing the result. Also it is, after all, acknowledged that, after decomposing this quantity of the two kinds of air, and making all the allowance they could for the phlogisticated air, or azote, in the dephlogisticated air,

they found fifty-one cubic inches of this kind of air more than they could well account for. This quantity therefore, and perhaps something more (since the operators were interested to make it as small as possible) must have been formed in the process. And when this kind of air, as well as inflammable (hydrogen gas) is decomposed together with dephlogisticated air (oxygen gas), nitrous acid is produced. The probability therefore is, that the acidifying principle, or oxygen, in the dephlogisticated air which they decomposed, was contained in that phlogisticated air (azotic gas), and that, had the process been conducted in any other manner, it would have assumed the form of nitrous acid. They acknowledged that, except when the inflammable air (hydrogen gas) was burned in the slowest manner, the water they produced had more or less of acidity."

The Doctor, at one time, believed that water was composed of oxygen and hydrogen. But as, on repeating the experiment of burning hydrogen in oxygen gas, he could not collect as much water as was equal in weight to the gases consumed; and as that, which he did obtain was mixed with nitrous acid, he was induced to change his opinion, and suppose the water was not generated, but deposited by the gases during

the combustion, and that the body formed was the nitrous acid.[1]

The antiphlogistians alleged, when the experiment was performed on a large scale, the deficiency of water was very trifling, and never more than might with propriety be attributed to the unavoidable loss to which such experiments were liable; and they supposed the nitrous acid, found in the water, proceeded from some azotic gas having been contained in the oxygen gas employed, and this the more especially, as no way had been discovered for procuring oxygen gas perfectly free from azotic gas.

The experiment alluded to by the Doctor, in the paragraph last read, justifies the reasoning of the antiphlogistians. An account of it is to be found in the eighth and ninth volumes of the Annales de Chimie.

The union of the two substances was effected by filling a balloon with oxygen gas, adding to it hydrogen gas in a small stream, and setting them on fire by passing the electric spark through them. To the balloon were connected reservoirs, called gazometers, containing the two gases. By certain contrivances, these were made to supply the balloon with fresh portions

[1] *Experiments and Observations*, Vol. III, pp. 43 et seq.

of the gases, as fast as the combination took place.

The experiment lasted 185 hours, and at the end of it there was collected of water 12 ounces, 4 gros and 45 grains French weight, and there remained in the balloon a quantity of gas.

By comparing the volume of the two gases before the combustion, with that of the gas remaining in the balloon, and making every necessary correction for the difference of temperature and pressure, it appeared, that 12 ounces 4 gros and 49.2270 grains of the gases had been consumed: the difference between this weight and that of the water is a mere trifle.

The water was perfectly pure: yet this was not owing to the oxygen gas being free from admixture; for by a preliminary experiment it was discovered, that 100 cubic inches of it contained three of azotic gas; and 467 French cubic inches of this substance were found in the balloon, at the end of the experiment.

The cause of the purity of the water was discovered by Mr. Seguin to be the slowness with which the combustion was conducted: for he has ascertained, that, with materials of the same kind, the nitrous acid may be formed merely by carrying on the combustion quickly, and by that means raising the temperature to the point at which azotic and oxygen gases act on each other.

This observation of Mr. Seguin has been confirmed by Messrs. Pelletier and Jacquin,[2] and also by Mr. Van Marum:[3] so that pure water has been obtained in more than one experiment.

But Dr. Priestley supposes the oxygen and phlogiston formed azotic gas in Mr. Seguin's experiment. Certain it is, there were 51.7440 French cubic inches of azotic gas found in the balloon at the end of the experiment, above what had been found in the oxygen gas before the combustion.

This quantity was supposed by Mr. Seguin to have been owing to atmospherical air from which the gazometers could not be completely emptied, before they were filled with the other gases: but whether this be the true reason or not, for the appearance of these 51.7440 cubic inches, they could not possibly have been formed in the manner supposed by Dr. Priestley.

The oxygen gas consumed weighed 6209.869 grains and ought according to the Doctor to have contained 620.9869 grains of oxygen or

[2] *Annales de Chimie*, Tome X, p. 140.

[3] *Ibid.*, Tome XII, p. 139. Mr. Van-Marum's words are, "Dans une de mes expériences la combustion du gaz hydrogène était très-lente, en employant trois heures et demie pour la consumption de mille pouces cubiques du gaz hydrogène, & l'eau produite par cette expérience n'avoit absolument point d'acide. Une autre fois la vitesse avec laquelle l'air entroit dans la ballon étoit à peu près d'un tiers plus grande, & alors l'eau produite contenoit de l'acide foiblement sensible."

the acidifying principle; but 51.7440 French cubic inches of azotic gas weigh only 22.9971 French grains. Nay the whole quantity of azotic gas, found in the balloon, was equal only to 207.55348 French grains; and yet, besides oxygen, it ought to have contained phlogiston and water.

In addition to these striking proofs of the inconsistency of his principles, it may be remarked, the phlogiston of the inflammable air (hydrogen gas) ought to have weighed more than the whole quantity of azotic gas.

In page 290 of Vol. I of his Experiments and Observations, there is a calculation on the supposition that phlogiston composes one half of hydrogen gas: And in page 535 of Vol. III he says, "Water seems to constitute about nine parts in ten of dephlogisticated air (oxygen gas), but there seems to be a much less proportion of it in inflammable air (hydrogen gas)."

The hydrogen gas expended in Mr. Seguin's experiment amounted to 1039.358 grains; and if the phlogiston be estimated at only one fifth of that weight, it will be 207.8716 grains, which is more than the weight of the whole azotic gas.

Since, therefore, the azotic gas could not have been formed by the oxygen and hydrogen, and since no other product was obtained than water, and the weight of this corresponded to that of

the two gases consumed, it may with safety be inferred that they formed water by their combination.

But, continues the Doctor, "The experiments which I made on the decomposition of these two kinds of air in *close vessels*, appear to me to be much less liable to exception, and the conclusion drawn from them is the reverse of that of the French philosophers."

In what respect his experiments were less liable to exception than those of the French chemists, is what I cannot comprehend. Theirs were performed on a very extensive scale; great care was taken to ascertain the degree of purity of the gases before combustion; and the apparatus was so constructed that the results could be determined with the greatest nicety. The Doctor's, on the contrary, were made with very trifling quantities of materials; their purity was not tried; and their weight was not accurately determined.

In one experiment, he employed such a quantity of the gases, as, he says, ought to have afforded a grain of water; but he collected only a quarter of a grain: in another, he ought to have got two grains, whereas he obtained only a grain and an half. And these are the experiments which he opposes to those of the French chemists, and from which he concludes, the

water is not equal to the weight of the gases consumed![4]

Satisfied, however, of the superiority of his experiments, the Doctor proceeds to give their results,

"When dephlogisticated and inflammable air (oxygen and hydrogen gases), in the proportion of a little more than one measure of the former to two of the latter, both so pure as to contain no sensible quantity of phlogisticated air (azotic gas), are inclosed in a glass or copper vessel, and decomposed by taking an electric spark in it, a highly phlogisticated nitrous acid is instantly produced; and the purer the airs are, the stronger is the acid found to be. If phlogisticated air (azotic gas) be purposely introduced into this mixture of dephlogisticated and inflammable air (oxygen and hydrogen gases), it is not affected by the process; though when there is a considerable deficiency of inflammable air (hydrogen gas), the dephlogisticated air for want of it will unite with the phlogisticated air, and, as in Mr. Cavendish's experiments, form the same acid. But since both kinds of air, viz. the inflammable and the phlogisticated (hydrogen and azotic) contribute to form the same acid they must contain the same principle, viz. phlogiston."

[4] *Experiments and Observations*, Vol. III, p. 45.

"If there be a redundancy of inflammable air in this process, no acid will be produced, as in the great experiment of the French chemists; but in the place of it there will be a quantity of phlogisticated air (azotic gas). A considerable quantity of water is always produced in these decompositions of air. But this circumstance only proves that the greatest part of the weight of all kinds of air is water. I have, in my experiments on terra ponderosa aerata (carbonate of barytes), demonstrated that water constitutes about half the weight of fixed air (carbonic acid gas)."

It has been already shown, that hydrogen gas can neither form azotic gas nor nitrous acid; but it may be worth while to point out the reasons for these results.

In the detail which is given of these experiments in the third volume of his Experiments and Observations, there is no notice of any preliminary attempts to ascertain the degree of purity of the gases; but it is there said, the oxygen gas used in the two trifling experiments formerly mentioned was got from the oxyd of manganese; and that employed in other experiments, during which the explosions were performed in a copper vessel, was sometimes got from the same source, and at others from the red oxyd of mercury by the nitrous acid, and from

the red oxyd of lead. Now it is well known, that all these substances in general contain azote.—The first does so, in so remarkable a degree, that the first portions of gas which it yields on being heated are frequently pure azotic gas. The second, being made with the nitrous acid, also contains some of it. And the third attracts it from the atmosphere, as the Doctor himself has discovered.

Mr. Cavendish ascertained by his experiments, that, if there be less hydrogen used than is necessary for the saturation of the oxygen, a quantity of nitrous acid is formed; and that, if azotic gas be added to the mixture, caeteris paribus, the quantity of acid is always increased; but, that if there be a superabundance of hydrogen, no acid is produced.

Hence the reason why the azotic gas was not affected in Dr. Priestley's experiment, seems to have been, he used as much hydrogen as, with the azote contained in the oxygen gas and not attended to, was sufficient for the whole oxygen.

It has been already made evident, that water cannot enter into the composition of oxygen and hydrogen gases in the proportion alleged by the Doctor; and by a little attention to the experiments with the carbonate of barytes it will clearly appear, there is not the smallest founda-

tion for the opinion that water is necessary for the constitution of carbonic gas.

The native carbonate of barytes was said, by Dr. Withering and others, not to yield its carbonic acid at any temperature to which it could be exposed: but Dr. Priestley found, that when the vapour of water was sent over it when red hot in an earthen tube, it afforded carbonic acid gas with the greatest rapidity, and in an equal quantity as when it was dissolved in the muriatic acid; while at the same time some of the water disappeared. He hence concluded, that water must be a constituent part of carbonic acid gas.

"Attending," says he, "to the water expended in the process, I found that I procured 330 ounce measures of fixed air (carbonic acid gas) with the loss of 160 grains of water. According to this, as the air weighed 294 grains, the water in the fixed air must have been 80 parts of 147 of the whole.

"In another experiment, having previously found that three ounces of the terra ponderosa (carbonate of barytes) yielded about 250 ounce measures of fixed air (carbonic acid gas), I attended only to the loss of water in procuring it, and I found it to be one fifth of an ounce in two successive trials. The quantity of fixed air (carbonic acid gas) would weight 225 grains,

and the water expended about 100 grains, so that in this experiment also the fixed air (carbonic acid gas) must have contained about one half of its weight of water." [5]

This calculation, however, cannot be depended upon; for the loss which the carbonate of barytes sustained was not examined, and the carbonic acid gas must have dissolved a quantity of water which it would deposite on returning to the temperature of the atmosphere.

To these objections, which were first made by Mr. Berthollet, the Doctor has returned, "I found very exactly how much fixed air (carbonic acid gas) a given quantity of this substance (carbonate of barytes) would yield by means of water, which appeared to be the very same that it yielded by solution in spirit of salt (muriatic acid), and that it yielded no air at all by mere heat without water. It was quite sufficient therefore to find how much water was expended in procuring any quantity of fixed air (carbonic acid gas) from this substance. And as there was no other source of loss of water besides the fixed air (carbonic acid gas), it could not but be concluded, that it entered into its composition as a necessary part of it, and in the proportion which I ascertained." [6]

[5] *Experiments and Observations*, Vol. I, p. 131.
[6] *Ibid.*, Vol. III, p. 557.

In this answer, he has entirely overlooked the property which carbonic acid gas has of dissolving water. Every chemist knows it has that property and in a greater degree at a high than at a low temperature. But the water is not necessary to the constitution of the gas, because it exists before the solution of the water; and it may be deprived of the water, by sulphuric acid or any deliquescent substance, and still remain carbonic acid gas.

Besides, Dr. Hope, now Professor of Chemistry in the University of Edinburgh, has discovered that the carbonic acid can be separated from the barytes, by exposing the compound to such a temperature as can be raised in a smith's forge.[7]

To be sure, the disengagement of the carbonic acid takes place at a lower temperature when water is used; but this is only a proof that the separation is promoted by the tendency which carbonic acid gas has to combine with water.

Hence then the celebrated experiments with the terra ponderosa aerata, or carbonate of barytes, afford no support to the Doctor's principles.

"The reason, no doubt," says the Doctor, in a note at the end of the pamphlet, "why, in the experiments of the French chemists, the water

[7] *Edinburgh Philosophical Transactions.*

they produced was not without acidity, whenever the flame they made use of was too strong, was that, in that case, more of the dephlogisticated air (oxygen gas) in proportion to the inflammable (hydrogen gas) was consumed, than when the flame was weak; so that the results of their experiments exactly coincide with those of mine."

When his experiments are accurately examined, they are found to confirm those of the French chemists; but the reasoning in the note which has been read cannot be admitted.

The appearance of flame attends the combination of an inflammable substance and oxygen, when both are in the state of gas:—It is owing to their union taking place at many points at the same time; but as the union depends as much on the one as on the other, a proportional quantity of each must be as necessary to exhibit a weak as a strong flame.

The Doctor further relates of his experiments, "When the decomposition of dephlogisticated and inflammable air (oxygen and hydrogen gases) is made in a glass vessel, a peculiarly dense vapour is formed, which the eye can easily distinguish not to be mere vapour of water; and if the juice of turnsole [8] be put into the vessel, it

[8] An European plant the juice of which is turned blue by ammonia.—Editor.

immediately becomes of a deep red, which shows that it was an acid vapour.

"Since the acid that I procured in this process was in considerable quantity, and no phlogisticated air (azotic gas) was present, (for in the last of my experiments I did not even make use of an air pump, but first filled the vessel with water, and then displaced it by the mixture of the airs), I do not see how it is possible to account for the formation of this acid but from the union of the two kinds of air; and it can hardly be supposed that, in the very same process, the decomposition of the same substances should compose others so very different from each other as *water* and spirit of nitre (nitrous acid). I think I have sufficiently accounted for the result of the experiments made by the French chemists on the common hypothesis, which supposes inflammable air to contain phlogiston; but I do not see how it is possible for them to explain mine on theirs, according to which there is no such principle in nature. Upon the whole, it does not appear to me that the evidence, either for the composition or the decomposition of water, is at all satisfactory; and certainly the arguments in support of an hypothesis so extraordinary, and so novel, ought to be of the most conclusive kind."

Having in some of his experiments emptied

the vessel in which the explosions were made of common air, by means of an air pump, the Doctor supposed it might be objected, that he could not entirely exhaust the vessel; and it is on that account he has mentioned, that in the last of his experiments he did not use an air pump: but the azote which occasioned the production of the dense acid vapour was contained in the oxygen gas which he employed.

The objections contained in this section to the conclusions drawn from the experiments which the antiphlogistians consider as proofs of the decomposition and recomposition of water are,

1. Finery cinder (black oxyd of iron) does not contain oxygen.

2. The weight of the water collected after burning inflammable and dephlogisticated airs (hydrogen and oxygen gases) is not equal to that of the airs consumed. And,

3. Either the water so obtained is mixed with nitrous acid, or a quantity of phlogisticated air (azotic gas) is formed.

The Doctor is of opinion,

1. That finery cinder (black oxyd of iron) consists of water and iron deprived of phlogiston.

2. That when a metallic calx containing oxygen is reduced in inflammable air (hydrogen gas), fixed air (carbonic acid gas) is formed by

the union of the oxygen with the phlogiston and water of the inflammable air. And,

3. That during the combustion of inflammable in dephlogisticated air (hydrogen in oxygen gas), the phlogiston and oxygen form, according to circumstances, nitrous acid or phlogisticated air (azotic gas); and the water obtained by the process is not generated, but from being a constituent part of the two airs is deposited on their union.

But from what has been stated in the review of this section it appears,

1. The same substance is formed by exposing iron to the steam of water, by burning iron in oxygen gas, and by heating iron filings mixed with red oxyd of mercury.

2. Hydrogen gas is obtained when the iron is changed by being exposed to the vapour of water; but there is none afforded when the change is effected by either of the other processes.

3. The carbonic acid, which has been found after the reduction of certain metallic oxyds in hydrogen gas, was previously contained in these oxyds.

4. The water which may be collected when hydrogen is burned in oxygen gas is exactly equal in weight to the two substances which disappear.

5. The azotic gas which has been burned in the residuum was contained in the gases before the combustion.

6. The nitrous acid, formed when the combustion was rapid, was owing to the union of azote with oxygen.

7. The experiments with terra ponderosa do not show that water is necessary to the constitution of the gases. And consequently from these it follows,

That when water is brought in contact with red hot iron it is resolved into two substances, one of which combines with the iron, while the other assumes the form of gas—and, That water may be reproduced by reuniting these substances.

The third section begins as follows:

"Having considered the evidence that has been alleged in support of the antiphlogistic theory, and found it to be insufficient, I shall in this section mention a few objections that may be made to it from other considerations.

"1. If inflammable air, or hydrogen, be nothing more than a component part of water, it could never be produced but in circumstances in which either water itself, or something into which water is known to enter, is present. But in my experiments on heating finery cinder (black oxyd of iron) with charcoal, inflammable air is produced, though, according to the new

theory, no water is concerned. According to this theory, finery cinder, called the oxyd of iron, consists of nothing besides iron and oxygen; and the charcoal, made with the greatest degree of heat that can be applied, is equally free from water; and yet when these two substances are mixed together, and exposed to heat, they yield inflammable air in the greatest abundance.

"This fact I cannot account for on the principles of the new theory; but nothing is easier on those of the old. For the finery cinder (the black oxyd) containing water, as one of its component parts, gives it out to any substance from which it can receive phlogiston in return. The water, therefore, from the finery cinder (black oxyd of iron) uniting with the charcoal makes the inflammable air (hydrogen gas), at the same time that part of the phlogiston from the charcoal contributes to revive the iron. Inflammable air (hydrogen gas) of the very same kind is procured when steam is made to pass over red-hot charcoal."

Although hydrogen be a constituent part of water it enters into the composition of many other bodies, and therefore the presence of water is not necessary to account for its production.

The particulars of the experiment are related in page 279 of the first volume of the Doctor's Experiments and Observations. "Having" says

he, made the scales of iron (black oxyd of iron), and also the powder of charcoal very hot, previous to the experiment, so that I was satisfied that no air could be extracted from either of them separately by any degree of heat; and having mixed them together while they were very hot, I put them into an earthen retort, glazed within and without, which was quite impervious to air. This I placed in a furnace, in which I could give it a very strong heat; and connected it with proper vessels to condense and collect the water which I expected to receive in the course of the process. But to my great surprise, not one particle of moisture came over, but a prodigious quantity of air, and the rapidity of its production astonished me; so that *I had no doubt* but that the weight of the air would have been equal to the loss of weight both in the scales (the black oxyd) and the charcoal; and when I examined the air which I repeatedly did, I found it to contain one tenth of fixed air (carbonic acid gas); and the inflammable air which remained when the fixed air was separated from it, was of a very remarkable kind, being quite as heavy as common air. The reason of this was sufficiently apparent when it was decomposed by means of dephlogisticated air (oxygen gas), for the greatest part of it was fixed air."

The Doctor now thinks this last mentioned

fixed air was not a constituent part of the inflammable air, but formed by the union of its phlogiston with the dephlogisticated air.

The reducing of wood to charcoal consists in separating the more volatile from the less volatile parts. This is done very imperfectly in common charcoal. The hydrogen especially is retained with so great force that the coal must be exposed to *an intense and long continued heat.*

It is not mentioned in the detail of the experiment, that the charcoal was previously exposed to the greatest degree of heat that could be applied, it is merely said it was made very hot, and that was very far from being sufficient.

Unglazed earthen vessels absorb moisture from the atmosphere very greedily, and it is scarcely possible to glaze accurately the inside of an earthen retort; at all events it is quite impossible, without breaking the retort, to know whether it has been perfectly done or not.

The charcoal, the iron scales (black oxyd), and the retort should all have been exposed separately to an intense and long continued heat, immediately before being used; the weight of the charcoal and iron before the experiment should have been compared with their weight after it; and the weight of the gases obtained instead of being guessed at, should have been accurately determined and compared with the

loss sustained by the mixture. The experiment is, in its present state, of no value.

Mr. Berthollet first objected to the experiment that hydrogen was with great difficulty separated from carbone, and the Doctor in reply to him has said in page 556 Vol. III of his Experiments and Observations, "How obstinately charcoal retains water, is easily ascertained. For Mr. Berthollet himself would say, that when any particular degree of heat would not make charcoal yield any more inflammable air, there was no more water retained in it than the same degree of heat was able with its assistance to decompose. But by the assistance of finery cinder (black oxyd of iron) with even a much less degree of heat, it yields inflammable air very copiously, just as if steam had been made to pass over it in that heat; and judging from evident appearances, there can be no doubt but that with a sufficient quantity of finery cinder, to supply it with water, all the phlogiston in the charcoal, exclusive of that which contributed to the revival of the iron, will be converted into inflammable air."

From this answer, the Doctor seems to have misunderstood Mr. Berthollet. He has not said that charcoal retains *water* obstinately, his words are "il paroît, par un grand nombre d'expériences que le charbon retient fortement de

l'hydrogène; aussi avons nous distingué le principe charboneux au carbone du charbon ordinaire."

The results of the Doctor's experiments may be accounted for in this manner. The carbonic acid gas was formed by the union of the oxygen in the oxyd of iron with the carbone in the charcoal; and the heavy inflammable gas proceeded from the solution of some carbone in hydrogen gas furnished either by the charcoal or moisture contained in the retort.

It can be no objection to this explanation, that the charcoal afforded an inflammable gas at a lower temperature when mixed with oxyd of iron than when used by itself. If the proportion of hydrogen be very small in comparison with that of the carbone, the compound is solid at even a very high temperature; but when the proportion of hydrogen is greater, it is easily made gaseous. In the foregoing experiment the proportion of carbone was diminished by the union of part of it with the oxygen of the oxyd of iron.

At all events the explanation offered by the Doctor cannot be a just one. It has been already shown the supposition respecting the composition of oxygen gas is unfounded, and that, even after admitting that supposition, finery cinder

cannot consist of water and iron deprived of phlogiston.

2. "Though the new theory," says the Doctor, "discards phlogiston, and in this respect is more simple than the old, it admits another new principle, to which its advocates give the name of *Carbone*, which they define to be the same thing with charcoal free from earth, salts, and all other extraneous substances; and whereas we say that fixed air consists of inflammable air and dephlogisticated air or oxygen, they say that it consists of this carbone dissolved in dephlogisticated air [see Examination of Mr. Kirwan, p. 79]. Mr. Lavoisier says [*ibid.*, p. 63], that, 'wherever fixed air has been obtained, there is charcoal.' They therefore call it the carbonic acid.

"But in many of my experiments large quantities of fixed air have been procured where neither charcoal, nor any thing containing charcoal, was concerned, or none in quantity sufficient to account for it. When the purest malleable iron is heated in dephlogisticated air (oxygen gas) or in vitriolic acid air (sulphurous acid gas), a considerable quantity of fixed air is formed. It is said that *plumbago* is contained in iron. But it is not found in malleable iron, and least of all in the *air* that is expelled from it. Fixed air is also produced by reviving minium

(red oxyd of lead) in inflammable air (hydrogen gas), and if charcoal of copper be heated in dephlogisticated air, a quantity of fixed air equal to nine tenths of the dephlogisticated air will be found. More than thirty ounce measures of the purest fixed air were by this means procured from six grains of this charcoal, which is made by the union of spirit of wine and this metal.

"Lastly, fixed air is procured in great abundance in animal respiration. It is true that fixed air is procured by exposing lime water to atmospherical air, but it is never procured by this means in air confined in any vessel. There must, for this purpose, be an open communication with the atmosphere. But fixed air will be procured in great abundance by breathing air contained in the smallest receiver, and especially if the air be dephlogisticated. It must therefore be formed by phlogiston, or something emitted from the lungs, uniting with the dephlogisticated air which it meets there. It may be said that since we feed in a great measure upon vegetables (and even animal food is originally formed from them) and this principle of *carbone* is found in all vegetables, this may be the substance that is exhaled from the lungs. But since in this process, it forms the same substance that inflammable air from iron does with dephlogisticated air, or oxygen, it must be the same thing with it; and then

this *carbone* will only be another name for phlogiston."

The objection, that carbone is a hypothetical being, was formerly made by Mr. Keir, and answered by Mr. Berthollet, "If there were no method, says he, of procuring distilled water, and that in the explanation of phenomena which are owing to that fluid, it was considered independently of the small quantity of salts which it holds in solution, would Mr. Keir look upon water as an hypothetical being of which no idea could be formed? Charcoal which has been well urged by the fire contains sometimes less than an hundredth part of foreign matter which has no influence on its combinations; sometimes it contains much more: abstraction is made of that part foreign to its properties, and to avoid circumlocution, the name of carbone is given to the charcoal considered in a state of purity.[9]

Notwithstanding what the Doctor has asserted, it is scarcely possible to obtain iron free from plumbago; and this, from the quantity of carbone which it contains, can, with a due proportion of oxygen, make nearly four times its weight of carbonic acid.

The carbonic acid gas procured by the revival of the red oxyd of lead has been already accounted for.

[9] *Annales de Chimie*, Tome X, p. 145.

Charcoal of copper, as Dr. Priestley calls it, is made by passing the vapour of alcohol or of oil of turpentine through a red hot copper tube: a great quantity of hydrogen gas is evolved and a black substance collects in the tube. Of 446 grains of this black substance obtained in one experiment, 28 grains were copper; and of 508 got by another, 19 grains were copper: the remainder when burned afforded carbonic acid gas.

These experiments prove that alcohol or spirit of wine and oil of turpentine contain hydrogen and carbone; and that copper can separate the carbone from the hydrogen. Charcoal of copper, therefore, is not a compound of spirit of wine and copper, but of carbone and that metal.

That carbonic acid is formed during respiration is most certain, and that it is so by the addition of something to the oxygen contained in the atmosphere is equally certain; but the Doctor has forgot when he says, "it forms the same substance which inflammable air from iron does with dephlogisticated air, or oxygen."

In page 285 of the first volume of his Experiments and Observations, when speaking of the carbonic acid gas obtained by burning the inflammable gas which is procured by passing the vapour of water over red hot charcoal, he says in the text. "That the fixed air (carbonic acid gas)

is not generated in this process, is evident *from there being no fixed air found after the explosion of dephlogisticated air (oxygen gas) and inflammable air from iron.*" And in a note at the bottom of the page he observes, "When I wrote this paper, I imagined that the fixed air, which was found on the decomposition of this inflammable air with dephlogisticated air, had been contained in the inflammable air. But it will appear, that it must have been formed by the union of phlogiston (or inflammable air) and dephlogisticated air, made by the explosion: though it is remarkable *that no fixed air is formed when the inflammable air from iron is used.*"

Besides in p. 562, Vol. III, he says of inflammable air from iron, "that it may not only be washed in lime water, but even be wholly decomposed by being fired together with dephlogisticated air, *without discovering any fixed air at all.*"

Therefore the identity of carbone and the supposed phlogiston has not been established.

The third objection is a repetition of what he has said before. "3d. The antiphlogistians always suppose azote, or phlogistated air, to be a simple substance, though I think abundant evidence has been given (and more will be found in my last memoir, printed in the Transactions of the Philosophical Society at Philadelphia),

that it is composed of phlogiston and dephlogisticated air."

The abundant evidence which has been given amounts to, an assertion that he has shown in a series of experiments that azotic gas is formed during the oxydation of iron; and the circumstance of 51.744 cubic inches of azotic gas, having been found in the residuum of the great experiment made by Mr. Seguin and others, above what had been discovered in the oxygen gas before the combustion.

It is scarcely necessary to remind you, the first is contradicted by his own experiments and those of Mr. Lavoisier; and that the last, cannot be accounted for on his principles, even after granting a number of unfounded suppositions.

It is the Doctor's object, in the memoir which is to be published in the fourth volume of the Transactions of the Philosophical Society of Philadelphia, to prove, that there is a greater quantity of oxygen in the atmosphere than is supposed by the antiphlogistians, and was formerly believed by the Doctor himself; and that some of the azotic gas found after the combustion of certain substances in atmospherical air, is formed by the union of their phlogiston with the oxygen of the atmosphere. But as the Doctor has not favoured us with a detail of his experiments, and as they bear the most striking marks

of not having been performed with accuracy, I will not take up your time with a review of them.

The Doctor then remarks,

"4. As to the *new nomenclature*, adapted to the new theory, no objection would be made to it, if it were formed, as is pretended, upon a knowledge of the real constitution of natural substances; but we cannot adopt one, the principles of which we conceive not to be sufficiently ascertained. For other objections to this nomenclature, I refer to the Preface to Mr. Keir's excellent Dictionary of Chemistry. However, whether we approve of this new language or not, it is now so generally adopted, that we are under the necessity of learning, though not of using it."

Although the new nomenclature is not strictly methodical, and its terms are rather uncouth and harsh, yet as, in as far as the state of our knowledge enables us to judge, it in general expresses either the properties or composition of bodies, I most heartily recommend it.

The Doctor sums up, "On the whole, I cannot help saying, that it appears to me not a little extraordinary, that a theory so new, and of such importance, overturning every thing that was thought to be the best established in chemistry, should rest on so very narrow and precarious

a foundation, the experiments adduced in support of it being not only ambiguous, or explicable on either hypothesis, but exceedingly few. I think I have recited them all, and that on which the greatest stress is laid, viz. that of the formation of water from the decomposition of the two kinds of air, has not been sufficiently repeated. Indeed, it requires so difficult and expensive an apparatus, and so many precautions in the use of it, that the frequent repetition of the experiment cannot be expected; and in these circumstances the practised experimenter cannot help suspecting the accuracy of the result, and consequently the certainty of the conclusion.

"But I check myself. It does not become one of a minority, and especially of so small a minority, to speak or write with confidence; and though I have endeavoured to keep my eyes open, and to be as attentive as I could to every thing that has been done in this business, I may have overlooked some circumstances which have impressed the minds of others, and their sagacity is at least equal to mine.

"The phlogistic theory is not without its difficulties. The chief of them is, that we are not able to ascertain the weight of phlogiston, or indeed that of the oxygenous principle. But neither do any of us pretend to have weighed *light*, or the element of *heat*, though we do not doubt

but that they are properly *substances*, capable, by their addition, or abstraction, of making great changes in the properties of bodies, and of being transmitted from one substance to another."

The experiments adduced in support of the antiphlogistic doctrine are neither ambiguous, nor explicable on either *hypothesis*, nor few.—Those of the French chemists were performed with the greatest care and nicety, and a few such are of more consequence than thousands made without a due regard to accuracy and precision; and if I mistake not it has been shown, that they cannot be explained on the Doctor's principles, and that his numerous experiments confirm theirs.

The experiment of the formation of water has been frequently repeated. It has been performed on a large scale by Mr. Monge, by Messrs. Lavoisier and Meusnier, by Messrs. Fourcroy, Vauquelin, and Seguin, by Messrs. Pelletier and Jacquin, and by Mr. Van Marum.

The Doctor deserves credit for his candour; but I confess I am rather surprised, that after having calculated the weight of phlogiston and oxygen, and supported a theory on the supposition of the calculations being right, he should state, as the chief difficulty attending that theory, the impossibility of ascertaining the weight of these supported substances.

However, if these substances or principles did actually exist, one or both of them would have weight; for charcoal, whether it be "very nearly pure phlogiston," or contains "the acidifying principle as well as phlogiston," can be weighed.

It has been shown, that the formation of carbonic acid gas by the burning of charcoal, cannot be explained on the Doctor's principles, if both the phlogiston and the oxygen have weight; and it will be found equally inexplicable if one of them be destitute of that property.

Let it first be supposed the phlogiston has no weight; and let it be again granted, that his experiment on the combustion of charcoal in oxygen gas was accurate. The oxygen in the consumed charcoal could weigh no more than seven grains; and these, added to the tenth part of the weight of oxygen gas, would make 8.947974 grains. One half of the weight of carbonic acid gas is supposed to be water, and consequently if the phlogiston has no weight, the other half ought to be owing to the oxygen. But there could not be more of this oxygen than 8.947974 grains, and these, with an equal quantity of water, ought to have formed only 17.895948 grains of carbonic acid gas, while the quantity said to have been obtained was 25.1150 grains.

On the other hand, if the oxygen be supposed

to be destitute of weight, and phlogiston to be heavy as the phlogiston could not exceed seven grains, the quantity of carbonic acid gas should have been fourteen grains.

Besides, the water in the oxygen gas ought, in either case, to have exceeded that supposed to be necessary for the constitution of the carbonic acid gas. What became of this excess? Why did it not combine with the one grain and quarter of unconsumed charcoal?

Although it is more than probable that light, and the cause which excites in us the sensation of heat or caloric, are bodies; yet their existence as such does not make a necessary part of the antiphlogistic doctrine.

As the different parts of this section have no immediate connection, it is unnecessary to make any recapitulation.

The following note is subjoined to the last section: "N.B. For answers to the objections of Mr. Lavoisier and Mr. Berthollet to some experiments of mine relating to this subject, I refer to the last edition of my Observations on Air, Vol. III, p. 554."

Such of these answers as were applicable to the objections, which have been laid before you, have been already considered.

I have now, Gentlemen, finished the reading and examination of Dr. Priestley's pamphlet.

Perhaps, from having been so particular, I have almost exhausted your patience; but I trust you will excuse me, as the fate of several important branches of chemical science is involved in that of this subject.

From the view which has been given of the different explanations of the phenomena of combustion it appears, that Becher's is incomplete; Stahl's, though ingenious, is defective; the antiphlogistic is simple, consistent, and sufficient; while Dr. Priestley's, resembling Stahl's but in name, is complicated, contradictory, and inadequate. You doubtless therefore will be inclined to prefer the antiphlogistic doctrine: Indeed you may adopt it with safety; for from being a plain relation of facts, it is founded on no ideal principle, on no creature of the imagination; it is propt by no vague supposition, by no random conjecture; it is dependent upon nothing whose existence cannot actually be demonstrated; whose properties cannot be submitted to the most rigorous examination; and whose quantity cannot be determined by the tests of weight and measure.

THE END.

CONNECTICUT COLLEGE LIBRARY
dc
540.1 P933
Considerations on the doctrine of phlogi
3 1839 001975360

Date Due

MAR 3 1 '52			

540.1
P933

136665

08-AZQ-623